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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 25°.[1]

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Having improved our methods of work[2] to a point where we feel confident of the correctness of our results to the second decimal place of the numbers expressing the osmotic pressures,[3] we determined to make a serious attempt to ascertain the temperature coefficient of the force. With this in view, it was decided to measure the pressures of cane sugar solutions, ranging in concentration from 0.1 to 1.0 *weight-normal*, at intervals of five degrees, from 0° to 30°. The earliest measurements (Series I.[4] and II.[5]) were discarded, because they were made while the method was still in a somewhat crude state and liable to yield results in which the errors might equal, or even exceed, any probable temperature coefficient. Series III.[6] and IV.,[7]

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon this subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425, and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266, and 325.

[2] THIS JOURNAL, **40**, 266 and 325.

[3] *Ibid.*, **40**, 4.

[4] *Ibid.*, **34**, 1.

[5] *Ibid.*, **36**, 39.

[6] *Ibid.*, **37**, 425.

[7] *Ibid.*, **38**, 175.

on the other hand, the former at 0° and the latter at temperatures between 4° and 5°, were carried out after some of the larger defects of the method had been remedied; and they have, on that account, been temporarily retained for purposes of comparison.[1] But these also will soon disappear from any discussion of the temperature coefficient of osmotic pressure, if we succeed, as we expect during the coming winter, in carrying through new series of measurements at precisely 0° and 5°. The proposed work at 10° and 15° has already been published.[2] The measurements   at 25° are given in the present paper, while those at 20° and 30° are already under way.

The results which were obtained at 25° are presented in this paper in the customary form, in a series of twenty-two tables. Tables I. to XX. contain the data pertaining to each of the duplicate determinations of the pressure of the usual ten concentrations of solution.   Table XXI. gives a summary of the results of each experiment, while Table XXII. presents the mean values of these results for each concentration.

An explanation of our methods of recording and of calculation may serve to forestall a possible criticism of some of the figures which appear in the tables. It will be noticed in Tables I. and II. that the rotation, in one case, is recorded as 12°.6, and in the other as 12°.8.   The difference, 0°.2, is due, not to differences in the ratios of water to sugar molecules, but mainly to the fact that the temperatures of the two solutions differed by nearly 9°, the temperature of one solution being 28°.5, and of the other 19°.8.   In a minor degree it is due to the fact that we do not attempt to read the polarimeter closer than 0°.05, so that a rotation of 0°.08 would be recorded as 0°.1, and one of 0°.18 as 0°.2, while rotations of 0°.02 and 0°.13 would be recorded as 0°.00 and 0°.15, etc.   We do not endeavor to determine the rotation of the solutions at the precise temperature at which the osmotic pressure is measured, since, for our purpose—the detection of loss in concentration while in the cell—it is only necessary that the two solutions which are compared, namely, the original one and that removed

[1] This Journal, **40**, 208.
[2] *Ibid.*, **39**, 667; **40**, 194.

from the cell after an experiment, shall be at the *same* temperature at the time of the polariscopic examination. Again, it will be noted that only one pressure of the atmosphere is given for each experiment. This is the *mean* pressure of the atmosphere during the whole time of the experiment. Each individual observation of osmotic pressure is corrected, of course, for the exact atmospheric pressure which prevailed at the time of reading the manometer. Any apparent slight discrepancies between the recorded volumes of the nitrogen in the manometer and the corresponding osmotic pressures are due to the practice of recording only to the second place of decimals, while in the actual computations, decimals in the third and fourth places are taken into account in order to calculate a little more precisely the mean osmotic pressure, the ratio of osmotic to gas pressure, etc. The practice, however, sometimes leads to discrepancies in the records which appear at first sight to be errors in arithmetic. An example of this will be found in Tables I. and II., where the recorded osmotic pressures are identical, 2.56 atmospheres, as are also the gas pressures, 2.43 atmospheres; and yet the ratio of osmotic to gas pressure in one case is 1.055, and in the other 1.051. For the reassurance of those who may have been disturbed by any seeming inconsistencies in the records such as have been pointed out, we wish to say that unusual care is taken to avoid errors in computation. In most cases, the results have been calculated independently by two individuals, and have then been revised by a third; and if any real errors have crept into the records, they have eluded the vigilance of not less than two computers.

In the first twelve of the twenty determinations of pressure at 25° (see Table XXI.), while the solutions were in the cells, there was no loss in concentration which could be detected by the polariscope. In this list are included the pressures of concentrations 0.1 to 0.6, inclusive. In seven of the eight remaining experiments, there was a slight loss in rotation, which, however, was small in comparison with the pressures measured. We have given in former papers our reasons for regarding this loss as due principally to a dilution of the cell contents which occurs *subsequent* to the measurement of pres-

sure, and which is, therefore, without effect upon the accuracy of the experiment. Accordingly, no correction for dilution has been applied in calculating the osmotic pressures which are recorded in the tables. Nevertheless, we have given, in each case where a loss in rotation was observed, the correction which would be applied if the loss were regarded as due to inversion. The maximum correction for any one concentration (the normal solution, see Table XX.) was 0.03 atmosphere in a total pressure of 26.33 atmospheres, which would not materially affect the ratio of osmotic to gas pressure.

Throughout the work, the temperature of the solutions did not deviate sensibly from 25°, while the temperature of the space occupied by the manometers differed only slightly from that of the solutions. The *"thermometer effects"* cannot, therefore, have been serious. However, we do not flatter ourselves that *thermometer effects* have been wholly eliminated, for the slight fluctuations which are observed after the pressure has reached a maximum we still believe to be due, as a rule, to small changes in the temperature of the solutions. The osmotic cell is also an extremely sensitive thermometer, and it is easily possible for it to indicate changes of temperature which would not be detected by the ordinary mercury thermometer, which is graduated in tenths of a degree.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 12°.6; (2) at conclusion of expr., 12°.6; loss, 0. *Manometer:* No. 13; volume of nitrogen, 432.33; displacement, 0.04 mm. Cell used, C₃. Resistance of membrane, 143,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.46; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.49. Time of setting up cell, 4.00 P. M., June 18, 1908.

Time.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 18.						
11.00 P.M.	25°.00	25°.00	140.31	2.56	2.43	0.13
June 19.						
10.00 A.M.	25°.00	24°.90	139.26	2.57	"	0.14
10.00 P.M.	25°.00	25°.10	140.42	2.56	"	0.13
June 20.						
10.30 P.M.	25°.00	25°.10	140.32	2.56	"	0.13
				2.56	2.43	0.13

Molecular osmotic pressure, 25.63.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.055.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 12°.8; (2) at conclusion of expr., 12°.8; loss, 0. *Manometer:* No. 20; volume of nitrogen, 415.91; displacement, 0. Cell used, B₃. Resistance of membrane, 225,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.42; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.12. Time of setting up cell, 5.00 P. M., Oct. 27, 1908.

Time.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Oct. 29.						
9.00 A.M.	25°.00	24°.90	133.62	2.55	2.43	0.12
4.30 P.M.	25°.00	24°.90	133.55	2.56	"	0.13
10.00 P.M.	25°.00	25°.00	133.51	2.56	"	0.13
Oct. 30.						
12.00 M.	25°.00	24°.95	133.30	2.55	"	0.12
				2.56	2.43	0.13

Molecular osmotic pressure, 25.55.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.051.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 24°.95; (2) at conclusion of expr., 24°.95; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, G. Resistance of membrane, 550,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.55; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.68. Time of setting up cell, 5.00 P. M., Oct. 24, 1908.

Time. Oct. 26.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
1.00 P.M.	25°.00	25°.10	85.57	5.08	4.86	0.22
5.00 P.M.	25°.00	25°.00	85.65	5.07	"	0.21
8.00 P.M.	25°.00	25°.00	85.24	5.10	"	0.24
Oct. 27.						
8.00 A.M.	25°.00	25°.00	85.21	5.09	"	0.23
				5.09	4.86	0.23

Molecular osmotic pressure, 25.43.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.046.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original 24°.95; (2) at conclusion of expr., 24°.95; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, D. Resistance of membrane, 550,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.47; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.86. Time of setting up cell, 5.00 P.M., Oct. 24, 1908.

Time. Oct. 25.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.30 A.M.	25°.00	24°.95	67.81	5.10	4.86	0.24
12.30 P.M.	25°.00	25°.00	67.77	5.10	"	0.24
9.00 P.M.	25°.00	25°.00	67.57	5.11	"	0.25
Oct. 26.						
1.00 P.M.	25°.00	25°.00	68.08	5.08	"	0.22
				5.10	4.86	0.24

Molecular osmotic pressure, 25.49.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.049.

Table V.

0.3 Wt. normal solution.   Exp. No. 1.   *Rotation:* (1) original, 36°.6; (2) at conclusion of expr., 36°.6; loss, 0.   *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.06 mm.   Cell used, B_3.   Resistance of membrane, 190,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02.   Initial pressure, 7.44.   Time of setting up cell, 4.00 P. M., June 30, 1908.

| Time. | Temperature. | | Volume N_2. | Pressure. | | |
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
July 1.						
10.00 A.M.	25°.00	25°.30	54.03	7.58	7.29	0.29
1.00 P.M.	25°.00	25°.40	54.05	7.57	"	0.28
11.00 P.M.	25°.00	25°.50	54.04	7.57	"	0.28
July 2.						
10.30 A.M.	25°.00	25°.10	54.01	7.58	"	0.29
				7.58	7.29	0.29

Molecular osmotic pressure, 25.27.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.040.

Table VI.

0.3 Wt. normal solution.   Exp. No. 2.   *Rotation:* (1) original, 36°.7; (2) at conclusion of expr., 36°.7; loss, 0.   *Manometer:* No. 13; volume of nitrogen, 432.33; displacement, 0.00.   Cell used, B_3.   Resistance of membrane, 275,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02.   Initial pressure, 7.35.   Time of setting up cell, 4.00 P. M., Oct. 24, 1908.

| Time. | Temperature. | | Volume N_2. | Pressure. | | |
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Oct. 25.						
9.30 A.M.	25°.00	24°.95	54.33	7.55	7.29	0.26
4.00 P.M.	25°.00	25°.00	54.24	7.56	"	0.27
10.00 P.M.	25°.00	25°.00	54.34	7.55	"	0.26
Oct. 26.						
9.00 A.M.	25°.00	25°.00	54.47	7.54	"	0.25
				7.55	7.29	0.26

Molecular osmotic pressure, 25.17.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.036.

Table VII.

0.4 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original 47°.9; (2) at conclusion of expr., 47°.9; loss, 0. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0. Cell used, B₃. Resistance of membrane, 104,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.14. Time of setting up cell, 5.00 P. M., May 29, 1908.

Time. May 30.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	25°.00	25°.00	38.73	10.10	9.72	0.38
12.00 M.	25°.00	25°.10	38.71	10.10	"	0.38
4.00 P.M.	25°.00	25°.10	38.78	10.09	"	0.37
12.00 P.M.	25°.00	25°.20	38.76	10.09	"	0.37
				10.10	9.72	0.38

Molecular osmotic pressure, 25.20.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.040.

Table VIII.

0.4 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 47°.95; (2) at conclusion of expr., 47°.95; loss, 0. *Manometer:* No. 13; volume of nitrogen, 432.33; displacement, 0. Cell used, D₃. Resistance of membrane, 366,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.30. Time of setting up cell, 4.00 P. M., Oct. 26, 1908.

Time. Oct. 27.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
12.00 M.	25°.00	25°.00	40.96	10.16	9.72	0.44
9.00 P.M.	25°.00	25°.05	41.13	10.12	"	0.40
Oct. 28.						
9.00 A.M.	25°.00	24°.95	41.14	10.12	"	0.40
5.00 P.M.	25°.00	24°.95	41.11	10.13	"	0.41
				10.13	9.72	0.41

Molecular osmotic pressure, 25.33.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.042.

Table IX.

0.5 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 58°.60; (2) at conclusion of expr., 58°.60; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.05 mm. Cell used, B_3. Resistance of membrane, 140,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.4. Time of setting up cell, 5.00 P.M., May 25, 1908.

Time. May 26.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	25°.00	25°.00	35.95	12.77	12.15	0.62
11.40 P.M.	25°.00	25°.10	36.01	12.76	"	0.61
May 27.						
9.00 A.M.	25°.00	25°.10	36.09	12.73	"	0.58
1.00 P.M.	25°.00	25°.20	36.09	12.73	"	0.58
				12.75	12.15	0.60

Molecular osmotic pressure, 25.50.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.049.

Table X.

0.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 58°.60; (2) at conclusion of expr., 58°.60; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.07 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.70. Time of setting up cell, 5.00 P. M., May 25, 1908.

Time. May 26.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	25°.00	25°.00	33.05	12.70	12.15	0.55
8.00 P.M.	25°.00	25°.60	33.03	12.72	"	0.57
May 27.						
9.00 A.M.	25°.00	25°.10	33.08	12.70	"	0.55
1.00 P.M.	25°.00	25°.20	33.05	12.71	"	0.56
				12.71	12.15	0.56

Molecular osmotic pressure, 25.42.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.046.

Table XI.

0.6 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 69°.0; (2) at conclusion of expr., 69°.0; loss, 0. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0. Cell used, Λ_3. Resistance of membrane, 50,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.19. Time of setting up cell, 5.00 P. M., May 25, 1908.

Time. May 26.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	25°.00	25°.00	25.65	15.43	14.58	0.85
8.00 P.M.	25°.00	25°.60	25.64	15.45	"	0.87
May 27.						
9.00 A.M.	25°.00	25°.10	25.67	15.43	"	0.85
1.00 P.M.	25°.00	25°.20	25.70	15.41	"	0.83
				15.43	14.58	0.85

Molecular osmotic pressure, 25.72.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.058.

Table XII.

0.6 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 69°.1; (2) at conclusion of expr., 69°.1; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, C_3. Resistance of membrane, 87,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.91. Time of setting up cell, 4.30 P. M., June 8, 1908.

Time. June 8.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	25°.00	25°.20	29.91	15.42	14.58	0.84
June 9.						
9.00 A.M.	25°.00	25°.10	29.93	15.41	"	0.83
11.00 P.M.	25°.00	25°.30	29.99	15.39	"	0.81
June 10.						
1.00 P.M.	25°.00	25°.20	29.95	15.41	"	'0.83
				15.41	14.58	0.83

Molecular osmotic pressure, 25.68.
Molecular gas pressure, 24.30.
Ratio of osmotic to gas pressure, 1.057.

Table XIII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 79°.2; (2) at conclusion of expr., 79°.1; loss, 0°.1 = 0.13 per cent. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, B_3. Resistance of membrane, 161,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.61. Time of setting up cell, 5.00 P. M., June 15, 1908.

Time. June 15.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
10.30 P.M.	25°.00	25°.10	25.70	18.01	17.02	0.99
June 16.						
10.00 A.M.	25°.00	24°.90	25.66	18.04	"	1.02
5.00 P.M.	25°.00	25°.00	25.67	18.03	"	1.01
June 17.						
10.00 A.M.	25°.00	24°.80	25.73	17.99	"	0.97
				18.02	17.02	1.00

Molecular osmotic pressure, 25.74.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.059.

Table XIV.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 79°.2; (2) at conclusion of expr., 79°.1; loss, 0°.1 = 0.13 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0. Cell used, A_3. Resistance of membrane, 60,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.84. Time of setting up cell, 5.00 P. M., June 15, 1908.

Time. June 15.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
10.30 P.M.	25°.00	25°.10	22.08	17.98	17.02	0.96
June 16.						
10.00 A.M.	25°.00	24°.90	22.03	18.03	"	1.01
5.00 P.M.	25°.00	25°.00	22.04	18.02	"	1.00
June 17.						
10.00 A.M.	25°.00	24°.80	22.06	17.99	"	0.97
				18.01	17.02	0.99

Molecular osmotic pressure, 25.73.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.058.

Table XV.

0.8 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 88°.8; (2) at conclusion of expr., 88°.8; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.03 mm. Cell used, B₃. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.64; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.9. Time of setting up cell, 5.00 P. M., June 6, 1908.

Time. June 7.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
1.00 P.M.	25°.00	24°.70	22.38	20.75	19.45	1.30
11.00 P.M.	25°.00	24°.80	22.38	20.74	"	1.29
June 8.						
10.00 A.M.	25°.00	24°.80	22.38	20.74	"	1.29
3.30 P.M.	25°.00	24°.90	22.38	20.75	"	1.30
				20.75	19.45	1.30

Molecular osmotic pressure, 25.94.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 88°.8; (2) at conclusion of expr., 88°.6; loss, 0°.2 = 0.23 per cent. *Manometer:* No. 13; volume of nitrogen, 432.33; displacement, 0.7 mm. Cell used, D. Resistance of membrane, 183,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.64; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.91. Time of setting up cell, 5.00 P. M., June 6, 1908.

Time. June 8.	Temperature.		Volume N₂.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
10.00 A.M.	25°.00	24°.80	20.54	20.71	19.45	1.26
3.30 P.M.	25°.00	24°.90	20.54	20.71	"	1.26
11.00 P.M.	25°.00	25°.20	20.54	20.71	"	1.26
June 9.						
9.00 A.M.	25°.00	25°.10	20.54	20.71	"	1.26
				20.71	19.45	1.26

Molecular osmotic pressure, 25.89.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.065.

Table XVII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 98°.5; (2) at conclusion of expr., 98°.35; loss, 0°.15 = 0.15 per cent. *Manometer:* No. 5: volume of nitrogen, 471.94; displacement, 0.02 mm. Cell used, B_3. Resistance of membrane, 138,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 20.74. Time of setting up cell, 5.00 P. M., June 3, 1908.

Time. June 4.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	25°.00	24°.9	19.62	23.70	21.88	1.82
9.00 P.M.	25°.00	24°.9	19.64	23.69	"	1.81
June 5.						
9.00 A.M.	25°.00	24°.9	19.64	23.68	"	1.80
3.00 P.M.	25°.00	24°.9	19.64	23.68	"	1.80
				23.69	21.88	1.81

Molecular osmotic pressure, 26.32.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.083.

Table XVIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 98°.4; (2) at conclusion of expr., 98°.15; loss, 0°.25 = 0.25 per cent. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.06 mm. Cell used, A_3. Resistance of membrane, 51,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.60; (3) dilution, 0.04; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 22.49. Time of setting up cell, 4.00 P. M., June 25, 1908.

Time. June 26.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
10.00 A.M.	25°.00	25°.20	18.05	23.61	21.88	1.73
5.00 P.M.	25°.00	25°.20	18.04	23.62	"	1.74
June 27.						
10.00 A.M.	25°.00	25°.00	18.04	23.62	"	1.74
1.00 P.M.	25°.00	25°.10	18.02	23.66	"	1.78
				23.63	21.88	1.75

Molecular osmotic pressure, 26.26.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.080.

Table XIX.

1.0 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 107°.1; (2) at conclusion of expr., 107°.0; loss, 0°.1 = 0.09 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.23 mm. Cell used, B₃. Resistance of membrane, 283,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 25.11. Time of setting up cell, 4.15 P.M., June 18, 1908.

Time. June 19.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.30 A.M.	25°.00	24°.90	15.18	26.33	24.31	2.02
5.00 P.M.	25°.00	25°.20	15.20	26.31	"	2.00
10.00 P.M.	25°.00	25°.10	15.20	26.32	"	2.01
June 20.						
10.30 A.M.	25°.00	25°.00	15.20	26.31	"	2.00
				26.32	24.31	2.01

Molecular osmotic pressure, 26.32.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.083.

Table XX.

1.0 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 107°.1; (2) at conclusion of expr., 106°.7; loss, 0°.4 = 0.36 per cent. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.08 mm. Cell used, A₃. Resistance of membrane, 257,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.64; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 25.67. Time of setting up cell, 4.15 P. M., June 18, 1908.

Time. June 19.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.30 A.M.	25°.00	24°.90	17.69	26.32	24.31	2.01
5.00 P.M.	25°.00	25°.20	17.68	26.36	"	2.05
10.00 P.M.	25°.00	25°.10	17.69	26.34	"	2.03
June 20.						
10.30 P.M.	25°.00	25°.00	17.70	26.33	"	2.02
				26.34	24.31	2.03

Molecular osmotic pressure, 26.34.
Molecular gas pressure, 24.31.
Ratio of osmotic to gas pressure, 1.084.

Table XXI.—*Summary of Results.*

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1 "	25°.00	0°.00	0.00	2.56	2.43	0.13	25.63	24.30	1.055
	"	0°.00	0.00	2.56	2.43	0.13	25.55	24.30	1.051
0.2 "	"	0°.00	0.00	5.09	4.86	0.23	25.43	24.30	1.046
	"	0°.00	0.00	5.10	4.86	0.24	25.49	24.30	1.049
0.3 "	"	0°.00	0.00	7.58	7.29	0.29	25.27	24.30	1.040
	"	0°.00	0.00	7.55	7.29	0.26	25.17	24.30	1.036
0.4 "	"	0°.00	0.00	10.10	9.72	0.38	25.20	24.30	1.040
	"	0°.00	0.00	10.13	9.72	0.41	25.33	24.30	1.041
0.5 "	"	0°.00	0.00	12.75	12.15	0.60	25.50	24.30	1.049
	"	0°.00	0.00	12.71	12.15	0.56	25.42	24.30	1.046
0.6 "	"	0°.00	0.00	15.43	14.58	0.85	25.72	24.30	1.058
	"	0°.00	0.00	15.41	14.58	0.83	25.68	24.30	1.057
0.7 "	"	0°.10	0.01	18.02	17.02	1.00	25.74	24.31	1.059
	"	0°.00	0.00	18.01	17.02	0.99	25.73	24.31	1.057
0.8 "	"	0°.10	0.01	20.75	19.45	1.30	25.94	24.31	1.067
	"	0°.20	0.03	20.71	19.45	1.26	25.89	24.31	1.065
0.9 "	"	0°.00	0.00	23.69	21.88	1.81	26.32	24.31	1.083
	"	0°.15	0.02	23.63	21.88	1.75	26.26	24.31	1.080
1.0 "	"	0°.25	0.04	26.32	24.31	2.01	26.32	24.31	1.083
	"	0°.40	0.05	26.34	24.31	2.03	26.34	24.31	1.084

Table XXII.—Summary of Results.   Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.
0.1	25°.00	0°.00	0.00	2.56	2.43	0.13
0.2	"	0°.00	0.00	5.10	4.86	0.24
0.3	"	0°.00	0.00	7.57	7.29	0.28
0.4	"	0°.00	0.00	10.12	9.72	0.40
0.5	"	0°.00	0.00	12.73	12.15	0.58
0.6	"	0°.00	0.00	15.42	14.58	0.84
0.7	"	0°.10	0.01	18.02	17.02	1.00
0.8	"	0°.10	0.015	20.73	19.45	1.28
0.9	"	0°.20	0.03	23.66	21.88	1.78
1.0	"	0°.20	0.03	26.33	24.31	2.02
				142.24	133.69	

Concentration.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	25.59	24.30	1.053
0.2	25.46	24.30	1.048
0.3	25.22	24.30	1.038
0.4	25.27	24.30	1.041
0.5	25.46	24.30	1.048
0.6	25.70	24.30	1.058
0.7	25.74	24.31	1.059
0.8	25.92	24.31	1.066
0.9	26.29	24.31	1.082
1.0	26.33	24.31	1.084

Tables XXIII. and XXIV. give a summary of the progress which has been made, up to the present time, in our attempt to ascertain the temperature coefficient of the osmotic pressure of cane sugar solutions.   The first of these (XXIII.) gives the pressures which were obtained in the vicinity of 0°, between 4° and 5°, at 10°, 15°, and, more recently, at 25°.   As stated in the beginning of this paper, the first two series (I. and II.) have been discarded because they were made while the method was still in a very imperfect condition, while Series III. and IV., at 0° and 4°–5°, are retained only until we are able to repeat them under the present improved conditions.   Series V., VI., and VII. were carried through after the method had been developed to a fairly satisfactory state.   It will be seen that the *total pressures* (horizontal line No. 1) increase with

Table XXIII.—Osmotic Pressures. Series III.–VII.

Concentration.	Series III. Pressures. 0°.	Series IV. Pressures. 4°–5°.	Series V. Pressures. 10°.	Series VI. Pressures. 15°.	Series VII. Pressures. 25°.
0.1	2.42	2.40	2.44	2.48	2.56
0.2	4.79	4.75	4.82	4.91	5.10
0.3	7.11	7.07	7.19	7.33	7.57
0.4	9.35	9.43	9.58	9.78	10.12
0.5	11.75	11.82	12.00	12.29	12.73
0.6	14.12	14.43	14.54	14.86	15.42
0.7	16.68	16.79	17.09	17.39	18.02
0.8	19.15	19.31	19.75	20.09	20.73
0.9	21.89	22.15	22.28	22.94	23.66
1.0	24.45	24.53	25.06	25.42	26.33
	131.71	132.68	134.75	137.49	142.24
	23.95	24.12	24.50	24.98	25.70
	22.29	22.65	23.09	23.50	24.30
	1.074	1.065	1.061	1.064	1.064
	1.73	1.45	0.22	0.10	0.20

1. Total pressures
2. Mean molecular osmotic pressures
3. Mean molecular gas pressures
4. Mean ratio of osmotic to gas pressure
5. Mean loss in rotation (per cent)

Table XXIV.—*Mean Ratios of Osmotic to Gas Pressures.*
Series III.–VII.

Concentration.	Series III. Ratios. 0°.	Series IV. Ratios. 4°–5°.	Series V. Ratios. 10°.	Series VI. Ratios. 15°.	Series VII. Ratios. 25°.	Series V–VII. Mean ratios.
0.1	1.085	1.060	1.056	1.053	1.053	1.054
0.2	1.074	1.045	1.043	1.045	1.048	1.045
0.3	1.064	1.041	1.038	1.040	1.038	1.039
0.4	1.049	1.042	1.037	1.040	1.041	1.039
0.5	1.055	1.043	1.040	1.046	1.048	1.045
0.6	1.056	1.059	1.050	1.055	1.058	1.054
0.7	1.070	1.060	1.058	1.058	1.059	1.058
0.8	1.074	1.067	1.069	1.069	1.066	1.068
0.9	1.091	1.081	1.073	1.085	1.082	1.080
1.0	1.097	1.084	1.085	1.083	1.084	1.084

rising temperature—from 131.71 atmospheres at 0° to 142.24 atmospheres at 25°. There is also, of course, a corresponding increase in the mean molecular osmotic pressures (horizontal line No. 2). The corresponding mean molecular gas pressures are given, for purposes of comparison, in horizontal line No. 3, while the mean ratios of osmotic to gas pressure, calculated from the aggregate pressure of each series (line No. 1) are recorded in line No. 4. The figures in this line (No. 4) will show at a glance how nearly the observed osmotic pressures appear to follow the law of Gay-Lussac for gases. If they obey the law, the ratios in question should be constant within the limits of necessary experimental errors. Except in the case of Series III.—the earliest of those which are included in the table—they are strikingly concordant. At 15° and 25°, they are identical.

In line No. 5 (Table XXIII.), the mean loss in rotation is given. It will be seen that this was relatively large in the earlier series (III. and IV.), and very small in the later ones (V., VI., and VII.). The loss in rotation is a fair measure of the excellence of the method, although, as we have pointed out elsewhere, it probably exceeds at all times the uncertainty of the results.

In Table XXIII., the aggregate of the pressures of each series has been treated as a unit because by so doing[1] "certain

[1] This Journal, **40**, 211.

discrepancies observable among the individual concentrations are prevented from obscuring the general trend of the values." Table XXIV. is introduced to show how the individual concentrations have been found to behave with respect to the ratio of osmotic to gas pressure. Here again the ratios for each individual concentration should be found to be constant, if osmotic pressure obeys the law of Gay-Lussac. A comparison of the figures in the horizontal lines will show that they differ but little among themselves except in the cases of the earliest series (III. and IV.). A particular discussion of the relations revealed in Table XXIV. will be postponed until we have completed the work at 20° and 30°, and have repeated Series III. and IV. We shall also repeat certain portions of the work at 10°, 15°, and 25°. This will be done wherever a ratio appears to differ markedly from the other ratios of the same concentration. An instance of this kind will be noted in the case of the 0.9 normal solution of Series V., where the ratio of osmotic to gas pressure was found to be 1.073 (see table), while the ratios at 4°–5°, 15°, and 25° are 1.081, 1.085, and 1.082. The method is already quite capable of testing the reality of such apparent discrepancies.

Johns Hopkins University,
November 1, 1908.

THE PRESENT STATUS OF THE SOLVATE THEORY.

[TWENTY-THIRD COMMUNICATION.]

By Harry C. Jones.

This work has been in progress continuously for ten years, and the results obtained published in various scientific journals. It now seems desirable to bring together in one compact whole the more important facts established, and the more important conclusions reached.

This entire work is the outcome, directly or indirectly, of an observation, made in 1898 by Jones and Ota,[1] that the molecular

[1] This Journal, **22**, 5 (1899).

lowering of the freezing point of water produced in concentrated solutions of certain electrolytes increases from a certain concentration, not only with the dilution, *but also with the concentration*.

This fact was directly at variance with the ideas which then prevailed in reference to the nature of solutions, and could be dismissed only with the unsatisfactory statement that the laws which obtain for dilute solutions do not hold for concentrated solutions, a statement which, of course, explained nothing. The fact that the molecular lowering of the freezing point increased with increase in concentration, and acquired a value in fairly concentrated solutions that was often much greater than the theoretical molecular lowering produced by the completely dissociated electrolyte, merited careful study. These results obtained by Jones and Ota were not published in their paper. Similar observations were, however, made a little later by Jones and Knight[1] in their study of aqueous solutions of double salts. They measured the freezing point lowerings produced by the three double chlorides—ammonium magnesium chloride, sodium zinc chloride, and strontium cadmium chloride—and from these results calculated the molecular lowerings. The following data[2] for two salts will show what was obtained:

$NH_4Cl.MgCl_2$.		$2NaCl.ZnCl_2$.	
Volume.	Molecular lowering.	Volume.	Molecular lowering.
1.92	9.48	3.03	12.27
3.84	8.71	6.06	11.84
7.68	8.52	12.12	11.71
15.36	8.63	24.24	11.84
30.72	8.89	48.48	12.47
61.44	9.31		
122.88	9.65		

The molecular lowerings are greater in the more concentrated solutions, decrease with increase in dilution to a minimum, and then increase from this point with the dilution. There is a minimum in the curve expressing the relation between

[1] This Journal, **22**, 128 (1899).
[2] *Ibid.*, **22**, 110 (1899).

concentration and molecular lowering of the freezing point.

Having established the existence of a minimum in the freezing point curve for a number of substances, Jones and Knight left this question here and continued the investigation of another problem upon which they were engaged, and to which the above line of work was at that time subordinate.

Sufficient observations had, however, been made to show that here was a phenomenon meriting careful study, and which would probably lead to something of importance if thoroughly investigated.

Work of Jones and Chambers.

Jones and Chambers[1] then took up this problem in a systematic manner. On examining the literature of freezing point lowerings produced in concentrated solutions, they found that a few observations were recorded which were similar in character to those made in this laboratory. Arrhenius[2] had shown that a few chlorides, such as those of calcium, strontium, and magnesium, and cadmium iodide, showed a minimum in the molecular lowering of the freezing point with change in concentration, and similar results had been obtained with three or four organic compounds, while Loomis[3] had discovered a corresponding minimum for hydrochloric acid and magnesium chloride.

We found that the number of cases where a minimum in the freezing point lowering had been observed was thus very small, and it was not even suspected that this was a general property of substances. Further, the cases observed were so isolated that no relation between this and any other property had been pointed out.

Jones and Chambers[4] raised these questions: "Are these apparently abnormal results peculiar to a substance here and there, regardless of its chemical nature, or are they confined to some group of compounds? Do substances which are chemically allied show this peculiarity?"

[1] This Journal, **23,** 89 (1900).
[2] Z. physik. Chem., **2,** 496 (1887).
[3] Wied. Ann., **57,** 503 (1896).
[4] This Journal, **23,** 92 (1900).

Since Jones and Knight had observed the minimum in the freezing point curves for one or two members of the calcium group, Jones and Chambers turned their attention to the chlorides and bromides of calcium, strontium, barium, magnesium, and cadmium. All of these substances, except the salts of cadmium, showed the minimum in the freezing point curves, at concentrations ranging from o.1 to o.2 normal.

The conductivities of these solutions were measured to see whether the conductivity curves showed any corresponding minimum. No such minimum was found.

Jones explained these results in the following words:[1] "How is it then possible to account for these abnormally great depressions of the freezing point? There appears to us to be only one way. In concentrated solutions these chlorides and bromides must take up a part of the water, forming complex compounds with it, and thus removing it from the field of action as far as freezing point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit, or as one molecule, in lowering the freezing point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all of the freezing point results obtained."

It was pointed out at this time[2] that practically all of those substances in which a freezing point minimum had been observed were strongly hygroscopic, *i. e.*, had the power to combine readily with water out of solution, and that there was probably a connection between this property and the power to combine with water when dissolved in it. It "should

[1] This Journal, **23**, 103 (1900).
[2] *Ibid.*, **23**, 104 (1900).

be observed, in connection with the explanation we have offered of these abnormal results, that the chlorides and bromides of the alkaline earths are, generally, very hygroscopic substances, resembling sulphuric acid in their power of attracting water. It may be due to this property that they combine with water to such an extent in concentrated solutions.''

When the above suggestion was made I had grave doubts whether it was the true explanation of the phenomena that had been observed, since at that time I was not at all a believer in hydration or combination between the solvent and dissolved substance. The above suggestion was made as the only rational explanation of the results that I could think of. "We[1] do not put forward the above suggestion to account for our results as a final statement of a theory, but only as tentative, and subject to modification as new facts are brought to light. It does, however, seem to account qualitatively for the experimental facts which have been brought to light.''

Work of Chambers and Frazer.

At the suggestion of Jones, and under his guidance, Chambers and Frazer[2] continued the work of Jones and Chambers. Impressed by the fact that it is hygroscopic substances which show a pronounced freezing point minimum, Chambers and Frazer studied other hygroscopic compounds, such as hydrochloric and phosphoric acids, sodium acetate, zinc chloride, strontium iodide, cadmium iodide, and copper sulphate.

All of the substances investigated showed a more or less pronounced minimum in the freezing point curve, and it will be recognized that all of them have more or less attraction for water—are, as we say, hygroscopic.

The conclusion reached by Chambers and Frazer was that the theory advanced by Jones and announced in the paper by Jones and Chambers accounted for all of the facts that they had discovered. They further added that this seemed to them to be the only reasonable explanation of these facts.

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[1] This Journal, **23**, 105 (1900).
[2] *Ibid.*, **23**, 512 (1900).

The earlier investigations, then, showed that the minimum in the freezing point curve was not an isolated phenomenon, limited to a few substances, but was manifested by a large number of compounds. The question then arose: Is the phenomenon a general one? Do substances in general give too great lowering of the freezing point in concentrated solutions?

Work of Getman.

To test this point Jones and Getman[1] took up the problem in a broad way, and measured the freezing point lowerings, conductivity, and refractivity of a fairly large number of typical compounds. These included: hydrochloric acid and the chlorides of lithium, ammonium, sodium, potassium, calcium, strontium, and barium; nitric acid and the nitrates of lithium, ammonium, sodium, and potassium; sulphuric acid and the sulphates of ammonium, sodium, and potassium; sodium and potassium carbonates; phosphoric acid and potassium dihydrogen phosphate; and sodium and potassium hydroxides.

The conclusion[2] drawn from this work was "that with but few exceptions electrolytes in general give abnormal molecular depressions of the freezing point. Among these exceptions are sodium, potassium, and ammonium nitrates, and potassium dihydrogen phosphate.

"Among the chlorides we observe that those of the second group in the Periodic System give greater molecular depressions than those of the first group."

It was pointed out that the conductivity curves for all of the substances included in this investigation are normal, showing nothing corresponding to the minimum in the freezing point curves. The refractivity curves were practically straight lines.

The few boiling point curves obtained showed also a more or less pronounced minimum. It was noted in this investigation that the *minimum in the boiling point curves was at a greater concentration than in the freezing point curves.* And

[1] Z. physik. Chem., **46**, 244 (1903).   Phys. Rev., **18**, 146 (1904).
[2] Z. physik. Chem., **46**, 244 (1903).

it was pointed out that this is just what would be expected if this minimum was due to hydration. At the higher temperature the hydrates would be less stable, and a greater concentration would, therefore, be required to produce enough hydration to show the minimum in the curve. We shall see later that this is a point of some importance in connection with the evidence for the existence of hydrates in aqueous solutions.

Through a Grant generously awarded by the Carnegie Institution, Jones and Getman[1] were enabled to extend their earlier work to a larger number and greater variety of substances. In their second investigation they included the chlorides, nitrates, and sulphates of manganese, nickel, copper, and aluminium.

Boiling point measurements were also made with potassium iodide, sodium iodide, ammonium iodide, cadmium iodide, and sodium bromide, in ethyl alcohol.

Up to this time the freezing point lowerings of forty-nine compounds had been studied, and only nine failed to show a minimum in the freezing point curves. A number of these nine substances, however, gave abnormally great depressions of the freezing point in concentrated solutions, so that nearly all of the substances investigated, with the exception of two or three sulphates which are obviously polymerized in concentrated solutions, since their molecular lowerings are less than the constant for water, show abnormally great lowerings of the freezing point in such solutions. A relation was discovered, at this stage of the work, which has proved to be of considerable importance in dealing with the whole problem of hydration in aqueous solutions. On comparing the molecular lowerings of the freezing point, as shown by the various substances, it was seen that there is a relation between the freezing point lowering produced by the different substances and the amounts of water with which they crystallize.

Those substances that crystallize with the largest number of molecules of water of crystallization give the greatest molecular lowering of the freezing point of water in concentrated solutions.

[1] This Journal, **31**, 303 (1904).

This relation is of fundamental importance as bearing on the hydrate theory; indeed, is one of the strongest arguments in its favor. Those substances that combine with the largest amounts of water out of solution—water of hydration—would be the substances which in solution would combine with the largest amounts of water—would form the most complex hydrates. These would, of course, be the substances which would give the greatest lowerings of the freezing point of water, since the combined water would be removed from the field of action as far as freezing point lowering is concerned.

The evidence for the existence of hydrates seemed, at this time, to be sufficiently well established to make it highly probable that dissolved substances in general combine with more or less of the water in which they are dissolved. It was then a matter of importance to determine, if possible, even the approximate amount of water with which various substances combine, and Jones and Getman attempted to make such calculations.

The molecular lowering was calculated from the observed lowering in the usual way—by dividing the actual lowering by the concentration in terms of normal. Since, however, in concentrated solutions there are not one thousand grams of water in a liter of solution, this must be taken into account. The specific gravities of the solutions were determined, and from these data and the concentrations the amount of water present in a liter of the solution was easily calculated.

The theoretical molecular lowering for a substance at the dilution in question could also be easily calculated. It was necessary to know only the dilution of the solution, and the dissociation at that dilution, and then to apply Raoult's law. The normal molecular lowering for a completely undissociated, unhydrated compound, or the freezing point constant for water, was taken as $1°.86$.

"The[1] calculated molecular lowering can now be compared directly with the corrected, observed molecular lowering. If there were no hydration these two values would be equal. The magnitude of the hydration is obtained as follows: The

[1] Carnegie Publication, No. 60, p. 28 (1907).

calculated molecular lowering is divided by the corrected molecular lowering found. This ratio multiplied by 1000 gives the amount of water present playing the rôle of solvent, if the quantity of the substance present was dissolved in 1000 grams of water.

"The difference between this amount of water and 1000 grams is the quantity that is in combination with the dissolved substance, under the conditions that obtain in the solution in question. For a number of reasons everything is referred to 1000 grams of the solvent. The theoretical freezing point constant is calculated for 1000 grams of the solvent, and by calculating the depression found for the same amount of the solvent, the two sets of results are comparable. Further, by referring everything to a constant amount of the solvent, the various results can be compared directly with one another.

"If we know the number of grams of water that have combined with the dissolved substance, the number of gram-molecules of water that have entered into combination is obtained by dividing the above value by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water in combination with one molecule of the dissolved substance, when the amount of substance present in a liter of the solution is dissolved in 1000 grams of water.

"In order[1] then to be able to calculate the approximate composition of the hydrates formed by any given substance, it is necessary to know the following quantities:

"The lowering of the freezing point produced by the dissolved substance.

"The conductivity of the solution as an approximate measure of its dissociation.

"The specific gravities of the solutions, in order to calculate the difference between 1,000 grams of water and the amount contained in a liter of the solution."

Even with all of this data it is, of course, possible to calculate only the approximate composition of the hydrates formed,

[1] Carnegie Monograph, No. 60, 28 (1907).

since there are some assumptions made that are only approximations. This is especially true, as has been repeatedly pointed out, for the law of Raoult, which, in all probability, holds only approximately for concentrated solutions. However, the results obtained for the various substances are, in all probability, of the right order of magnitude, and show, at least, the correct relative hydrating power of the various compounds.

At this time Jones and Getman calculated, on the above basis, the approximate composition of the hydrates formed by salts of copper and aluminium. The complexity of the hydrates formed by these salts was found to be great—as much as forty or fifty molecules of water combining with one molecule of the salt. The most interesting fact brought out by these calculations was that the complexity of the hydrate increases with the dilution of the solution, and with fair regularity from the most concentrated to the most dilute solution investigated. This is, of course, just what would be expected from the law of mass action applied to the formation of these hydrates—the larger the amount of water present per molecule of the dissolved substance, the greater the amount of water combined with a dissolved molecule or the resulting ions.

Having found that water combines with a large number of dissolved substances, the question arose: Is this property limited to water? Do we have only hydration, or do other solvents also have the power of combining with substances dissolved in them?

Jones and Getman[1] extended their work from aqueous to nonaqueous solutions. They worked with solutions of lithium chloride, lithium nitrate, and calcium nitrate in ethyl alcohol, using the boiling point method, and plotted their results against concentrations as abscissae and molecular rise in the boiling points as ordinates.

Their work furnished evidence that the alcohol combines with the dissolved salt—that alcoholates are formed. The evidence furnished was, however, purely qualitative, the

[1] This Journal, **32**, 338 (1904).

results obtained not enabling them to calculate even the approximate composition of the alcoholates.

Having studied a few salts in a solvent other than water, and a large number of salts in water, Jones and Getman[1] took up the problem of nonelectrolytes and organic acids, to see whether these substances combine with any appreciable amount of water when dissolved in that solvent.

The results obtained are perfectly clean cut. Of thirteen nonelectrolytes, only one, glycerol, had any very marked power to combine with water. Glycerol has large hydrating power. A few other nonelectrolytes, such as cane sugar and fructose, also have some considerable power to combine with water, but this is not of the same order of magnitude as that shown by glycerol.

"The question as to whether the alcohols have any very marked hydrating power is of interest in the light of the composition which has been assigned to these hydrates by certain investigators."

It was found that while methyl and ethyl alcohols have slight power to combine with water, this is very small in comparison with the hydrating power of many salts.

It having been shown that certain of the strong mineral acids have considerable power to combine with water, the question arose: Is this power possessed by the organic acids? A number of them were studied from the standpoint of hydration, and it was found that none of them had any appreciable power to combine with water. In comparison with the mineral acids, the hydrating power of the organic acids is negligible. If the hydrating power of mineral acids is due to the hydrogen ions, which is questionable, then the organic acids have but little hydrating power because there are only a few hydrogen ions present—because they are only little dissociated.

A fairly broad discussion of the subject of hydration in general, as worked out by Jones and Getman, was prepared just before Dr. Getman left this laboratory.[2] The work was sufficiently extended by this time to make it possible to see

[1] Carnegie Monograph, No. 60, 101 (1907).
[2] Z. physik. Chem., **49**, 385 (1904).

the real significance and importance of the relation between freezing point lowering and water of crystallization. Nearly seventy compounds had been studied—salts of potassium, sodium, lithium, ammonium, calcium, strontium, barium, magnesium, zinc, cadmium, manganese, nickel, cobalt, copper, aluminium, chromium, and iron.

A number of these salts, notably those of potassium and ammonium, crystallize without water. Some of the sodium salts are anhydrous, while others crystallize with water. The salts of barium crystallize with two molecules of water; those of calcium, strontium, magnesium, nickel, and cobalt, with six molecules of water each, while the nitrates of aluminium, chromium, and iron crystallize with from eight to nine molecules of water.

Here then was an excellent opportunity to test the relation between freezing point lowering and water of crystallization. The curves expressing the relation between concentration and freezing point lowering were plotted; the chlorides on one sheet, the bromides on a second sheet, the iodides on a third, and the nitrates on a fourth.[1]

On the chloride sheet, all of those chlorides were introduced whose curves could be inserted without undue crowding. At the bottom of the sheet fell those chlorides that crystallize without water—potassium, sodium, and ammonium—and the three curves corresponding to these compounds were almost coincident. The chloride of lithium, a binary electrolyte with two molecules of water of crystallization, came next above, and then the chloride of barium, a ternary electrolyte with two molecules of crystal water.

Above the curve corresponding to barium chloride, and some distance above it, fell the curves for strontium, calcium, and magnesium chlorides, each crystallizing with six molecules of water. These three chlorides, again, ran close together.

Much farther above on the same sheet we find the chlorides of aluminium and iron—quaternary electrolytes, each crystallizing with six molecules of water.

The relation, then, between water of crystallization and

[1] Carnegie Publication, No. 60, p. 21 (1907).

lowering of freezing point was nearly perfect, as far as the chlorides were concerned.

The bromides, as already stated, were plotted on a corresponding sheet. The anhydrous bromides of cadmium and potassium fell near the bottom of the sheet. Sodium bromide with two molecules of water was somewhat above the bromide of potassium. The curve for lithium bromide was considerably above that of sodium.

Barium bromide—a ternary electrolyte with two molecules of water—occupies a considerably higher position on the sheet than lithium bromide, while for the bromides of strontium, calcium, and magnesium, each with six molecules of water of crystallization, the curves are close together and well above that of the bromide of barium.

The relations for the bromides are, then, as satisfactory as for the chlorides.

Exactly similar relations are shown on the iodide sheet. The curves for the anhydrous iodides of cadmium and potassium are at the bottom; that for sodium iodide, with two molecules of water, next above; and still higher is the curve for lithium iodide with three molecules of crystal water. The curve for the ternary iodide of barium, with its two molecules of water of crystallization, lies considerably above that for lithium iodide, while at the top of the sheet we have the curves for the iodides of strontium and calcium, each crystallizing with six molecules of water.

The curve sheet for the nitrates is even more convincing, if possible, than those already considered because of certain facts in connection with the nitrate of calcium, which will be considered below.

The curves for the anhydrous nitrates of sodium, potassium, and ammonium fall together at the bottom of the sheet. Then comes lithium nitrate with two molecules of water, and then the nitrate of calcium, which crystallizes with four molecules of water. The ternary nitrate of calcium, with four molecules of water, lies almost exactly half way between lithium nitrate with two molecules and a number of nitrates,

each with six molecules of crystal water. This relation is, certainly, most satisfactory.

The nitrates of manganese, cobalt, nickel, zinc, and magnesium all crystallize with six molecules of water, and their curves all occupy very nearly the same position on the nitrate curve sheet. The curve for the nitrate of copper is a little higher than would be expected.

The nitrates of aluminium, iron, and chromium crystallize, the first with eight, and the last two with nine molecules of water each. Their curves are very near the top of the sheet, lying far above those of any other nitrate studied. It should be noted that these salts not only crystallize with a larger amount of water than any other nitrates brought within the scope of this investigation, but are also quaternary electrolytes.

So much for the relations between the *different salts of the same acid with different metals*. Certain relations of equal interest and importance were found to exist *between the salts of the same metal with different acids*.

"If[1] we compare the results for the chlorides, bromides, iodides, and nitrates, we shall find abundant evidence bearing on the relation between freezing point lowering and water of crystallization. Chlorides, bromides, iodides, and nitrates that crystallize without water all show a molecular lowering of between 3 and 4, and this increases very slightly, if at all, with the concentration. As far as the comparison can be carried, lithium chloride, with 2 molecules of water, gives less lowering than lithium bromide or lithium iodide with 3 molecules of water, and just about the same lowering as lithium nitrate with 2 molecules of water of crystallization.

"Lithium bromide, with 3 molecules of water, gives about the same lowering as lithium iodide, which has the same amount of water of crystallization. Sodium bromide, with 2 molecules of water, gives very nearly the same lowering as sodium iodide, which has the same number of molecules of water of crystallization.

"Barium chloride has the same number of molecules of water

[1] Carnegie Monograph, No. 60, p. 25 (1907).

of crystallization as the bromide and iodide. Since barium chloride has only a slight solubility in water, comparison of freezing point lowerings must be limited to dilute solutions. The freezing point lowerings of the three salts are just about the same in the dilute solutions, although in the more concentrated solutions the iodide shows greater lowering than the bromide.

"If we compare the chlorides, bromides, and iodides of the alkaline earths, which contain each 6 molecules of water of crystallization, we shall find that the lowerings of the freezing point produced by them are all of the same order of magnitude. We shall, however, see that the bromides give somewhat greater lowering than the chlorides, and the iodides even greater lowering than the bromides.

"As far as comparisons can be made it seems that the nitrates produce about the same lowerings as the corresponding chlorides with an equal number of molecules of water of crystallization, and, therefore, somewhat less than the corresponding bromides and iodides.

"The quaternary chlorides of aluminium and iron can not be compared, at present, with respect to their freezing point lowering, with the corresponding bromides and iodides, because the latter have not yet been investigated.

"A comparison of the lowerings produced by the chlorides of iron and aluminium, containing 6 molecules of crystal water, with the nitrates of the same metals which have a larger amount of water of crystallization will show a somewhat greater lowering, at the same concentrations, for the nitrates.

"*Thus, the relation between the lowering of the freezing point of water produced by salts and their water of crystallization comes out on every hand, whether we compare the salts of a given acid with different metals, or the salts of the same metal with different acids.*"

Since, as will be seen later, Jones and Bassett call attention to the large number of examples illustrating the fact that water of crystallization is a function of the temperature at which the salt crystallizes, it might be concluded that the

above relations are not strictly true, but depend upon the temperatures at which the salts crystallize. That this is not the case will be seen if we consider that the amounts of water of crystallization attributed to the compounds are the amounts with which the several salts crystallize under ordinary conditions, *i. e.*, under as nearly comparable conditions as possible, and which are, therefore, directly comparable with one another.

Work of Bassett.

Jones and Bassett[1] plot the results referred to above in the form of curve sheets—the chlorides upon one sheet, the bromides upon another, the iodides upon a third, and the nitrates upon a fourth. An examination of these curve plates will bring out at a glance the relation between water of crystallization and lowering of the freezing point. Concentrations are plotted as the abscissae and molecular lowerings of the freezing point as the ordinates. The relative positions of the curves upon any one sheet, corresponding to the several salts of a given acid, are conditioned by the number of molecules of water with which the various salts crystallize.

The relations are so satisfactory and general that it would be a simple matter to determine quite closely the number of molecules of water with which an unknown chloride, for example, crystallizes, by determining its molecular lowering of the freezing point of water.

This line of evidence bearing upon the hydrate theory, as advanced by Jones, is so satisfactory and general, that it is regarded as a strong argument in favor of the general correctness of this theory.

The work of Jones and Bassett had to do primarily with the determination of the approximate composition of the hydrates formed by a large number of substances. They were able to calculate, more accurately than had hitherto been done, the composition of the hydrates, and found that the complexity of the hydrates increased with the dilution of the solution, as would be expected from the law of mass action.

[1] This Journal, **33**, 536–539 (1905). Jones: J. Chim. Phys., **3**, 478–481 (1905).

In general a fairly regular increase was observed; indeed, as regular as could be expected, considering the large number of experimentally determined values involved in each of these calculations, and, therefore, the large number of experimental errors which were necessarily introduced. These errors would be of a very considerable order of magnitude, especially in the more dilute solutions.

Jones and Bassett, in their earlier work, pointed out another line of evidence bearing upon the hydrate theory. If hydrates exist in solution they become more and more unstable with rise in temperature. This is characteristic of exothermic reactions in general, and is shown to apply to hydrates by the fact that at the boiling points of saturated solutions practically all of the water is removed, except that with which the compound crystallizes at the temperature in question.

The converse of the above can readily be tested by experimental facts. *These hydrates become more and more stable the lower the temperature*; consequently, dissolved substances would crystallize with more and more water the lower the temperature at which the crystals form.

That such is, in general, true is well known to every one; but how general such a relation is may not be fully appreciated by those who have not looked closely into the facts.

Jones and Bassett[1] examined the literature to see how many cases had been studied in this connection, and were surprised at the large number of striking examples upon record. A few examples will make this clear:

Salt with water of crystallization.	Temperature of crystallization.
$MgCl_2.12H_2O$	$—10°$ to $—12°$
$MgCl_2.10H_2O$	$+20°$
$MgCl_2. 8H_2O$	Above $+20°$
$MgCl_2. 6H_2O$	Higher temperatures
$MnCl_2.12H_2O$	$—48°$
$MnCl_2.11H_2O$	$—21°$ to $—37°$
$MnCl_2.6H_2O$	$—21°$
$MnCl_2.4H_2O$	$+15°$
$MnCl_2.2H_2O$	$+20°$

[1] Z. physik. Chem., **52**, 1231 (1905).

Salt with water of crystallization.	Temperature of crystallization.
$Ni(NO_3)_2.9H_2O$	$-27°$
$Ni(NO_3)_2.6H_2O$	$-16°$
$Ni(NO_3)_2.3H_2O$	$+58°$ and higher
$CO(NO_3)_2.9H_2O$	$-29°$ to $-22°$
$CO(NO_3)_2.6H_2O$	$-22°$ to $+56°$
$CO(NO_3)_2.3H_2O$	$+56°$ to $+91°$
$FeCl_3.6H_2O$	$-16°$ to $+20°$
$FeCl_3.3\frac{1}{2}H_2O$	$+20°$
$FeCl_3.2\frac{1}{2}H_2O$	$+40°$ to $+60°$
$FeCl_3.2H_2O$	$+60°$ to $+80°$
$FeCl_3$.anhydrous	$+80°$ and above

These examples suffice to illustrate the point and to show how regularly water of crystallization decreases with rise in temperature, just as would be expected from the hydrate theory. So far as is known to us, there is not a single exception to this relation on record.

Jones and Bassett carried out experiments which made it highly probable that some very well-known compounds can be made to crystallize with larger amounts of water than had been hitherto supposed possible, by crystallizing them at very low temperatures. These results have not yet been recorded, and will not be until further experimental work on these substances is completed.

Jones and Bassett raise the question as to whether it is the ions or the molecules that form hydrates. Since it had been shown by Jones and Getman that certain nonelectrolytes, such as glycerol, acetamide, fructose, etc., can combine with water, and since such substances in solution are undissociated, it follows that molecules have the power to combine with water.

Since, however, the magnitude of the hydration increases with the dilution of the solution, acquiring a very large order of magnitude in solutions so dilute that they contain mainly ions and only a few molecules, it follows not only that ions have great hydrating power, but in all probability, much greater hydrating power than the molecules. That mole-

cules have hydrating power is further shown by the fact that salts crystallize with water, which is essentially water of hydration. Substances under these conditions are chiefly in the molecular condition, unless we assume that the molecules are sufficiently dissociated in their own water of crystallization to yield enough ions to combine with all of the water brought out of solution as water of crystallization, which is highly improbable.

We must, then, conclude that both molecules and ions can form hydrates, but that the ions have much greater power to combine with water than the molecules when dissolved in that substance.

The nature of the hydrates formed by both electrolytes and nonelectrolytes was discussed by Jones and Bassett. In the hydrates formed by a substance like calcium chloride, for example, the number of molecules of water per molecule of the salt varies all the way from a few to a large number— at least as many as thirty.

This raises the question as to whether we have *all intermediate stages* represented, *i. e.*, a series of hydrates ranging in composition from a very few to at least thirty molecules, as appears from the results to be the case; or whether we have *a few definite hydrates*, and then mixtures of these in varying proportions.

It is impossible at present to decide finally between these two alternatives, since there is apparently no experimental method available for doing so directly. Under these conditions we accept the simpler alternative and regard the hydrates as having all compositions intermediate between the simplest and the most complex. Further, this view, it seems to me, is more in accord with the general properties of solutions, and the *regular changes* which are manifested in such properties as we change the dilution of the solutions.

The *stability of the hydrates* is not sufficiently great to justify us in calling them definite chemical compounds. It is well known that the more complex hydrates readily break down with rise in temperature, and marked decomposition results from slight changes in temperature, even when such

changes take place at comparatively low temperatures. We would, therefore, scarcely be justified in calling such unstable systems as the hydrates definite chemical compounds.

The later work of Jones and Bassett[1] had to do primarily with the determination of the composition of the hydrates formed by a fairly large number of salts, acids, and bases.

Among the salts are such compounds as chromium chloride, potassium ferrocyanide, potassium ferricyanide, sodium chromate, sodium dichromate, disodium phosphate, ammonium sodium acid phosphate, ammonium cupric chloride, potassium cupric chloride, etc.

Some results were obtained bearing on the way in which potassium ferro- and potassium ferricyanide dissociate.

A number of acids, such as hydrochloric, hydrobromic, nitric, phosphoric, and chromic, were included in this investigation, and also the bases, sodium hydroxide, potassium hydroxide, and ammonium hydroxide.

At the completion of the work of Jones and Bassett, about *one hundred compounds* had been brought within the scope of this investigation as a whole, and about *fifteen hundred solutions* had been worked with. All of the results thus far obtained were found to be in accord with the hydrate theory as proposed by Jones.

Work of West.

An unexpected line of evidence bearing upon the hydrate theory was brought to light by the work of Jones and West[2] on the temperature coefficients of conductivity, as was pointed out by Jones.[3] The conductivity of electrolytes increases rapidly with rise in temperature, as is well known. This is not due to any increase in dissociation with rise in temperature; on the contrary, the dissociation of electrolytes decreases as the temperature is raised. The large positive temperature coefficients of conductivity of electrolytes is then due to the increased velocity with which the ions move at the more elevated temperatures. There are a number of

[1] This Journal, **34**, 291 (1905).
[2] *Ibid.*, **34**, 357 (1905).
[3] *Ibid.*, **35**, 445 (1906).

factors coming into play which condition the velocities with which the ions move under a constant driving force. The chief factors would be the size and mass of the ions, and the viscosity of the medium in which they move. At the more elevated temperature the viscosity of the medium would become less and less, and this alone would tend to cause the ions to move the faster, the higher the temperature.

Another factor of great importance as conditioning the temperature coefficients of conductivity is the *decreasing complexity of the hydrate around the ion with rise in temperature*. Since the ion must drag this solvate with it through the solvent, the effect of decreasing the complexity of the solvate would be to decrease the mass of the ion, and, therefore, to increase its velocity.

This conclusion, which is a necessary consequence of the hydrate theory and the instability of hydrates with rise in temperature, can be tested directly by the experimental results obtained by Jones and West.

If the diminishing complexity of the hydrate formed by the ion with rise in temperature plays any important part in conditioning the large temperature coefficient of conductivity, then those ions that form the most complex hydrates would be the ones whose masses would change to the greatest extent with rise in temperature, since the more complex the hydrate the greater the change in its complexity for a given rise in temperature. In a word, *those ions that have the greatest hydrating power would have the largest temperature coefficients of conductivity.*

If we examine the results obtained by Jones and West, we shall see that the above conclusion is strikingly substantiated by the facts.[1] It will be recalled that hydrating power is nearly a linear function of the water of crystallization. Those compounds with the largest amounts of water of crystallization have much larger temperature coefficients of conductivity than those that crystallize with but little or no water.

[1] This Journal, **35,** 448 (1906).

A corollary to the above conclusion would be that those substances which have approximately the same hydrating power, *i. e.*, which crystallize with the same number of molecules of water, would have approximately the same temperature coefficients of conductivity. This conclusion is also abundantly verified by the facts. If we examine the temperature coefficients obtained by Jones and West, we see that those substances which crystallize with the same amounts of water have temperature coefficients of conductivity of at least the same order of magnitude, and in many cases are very nearly equal.

Since there are other factors than hydration coming into play as conditioning these temperature coefficients, such as the mass and volume of the unhydrated ion, the above agreements between fact and theory are as close as common sense would lead us to expect.

A second conclusion from the hydrate theory, as bearing upon temperature coefficients of conductivity, can also be tested by the results obtained by Jones and West.

The *more dilute the solution the more complex the hydrates existing in solution.* The more complex the hydrates the greater the change in the complexity with rise in temperature, as we have seen. If the temperature coefficients of conductivity are conditioned to any appreciable extent by the complexity of the hydrates, then the *more dilute solutions of a given substance should have larger temperature coefficients of conductivity than the more concentrated.*

That such is the case is seen at once by examining the temperature coefficients for any substance at different dilutions. The temperature coefficients become larger and larger the more dilute the solutions, until at a dilution of a thousand liters they are often nearly twice as large as the coefficients for the same substance at two liters, for example.

The conclusions from the hydrate theory are thus substantiated most satisfactorily by the experimental results, and this is, therefore, another line of evidence in favor of the general correctness of the theory.

Work of McMaster.

The work of Jones and McMaster,[1] as bearing on the theory of solvation in solution, is an extension of the work of Jones and Getman, and deals with solutions of certain salts in methyl and ethyl alcohols. The salts in question are lithium chloride, lithium bromide, and lithium nitrate in methyl and in ethyl alcohols, and calcium nitrate in ethyl alcohol. The boiling point method was employed.

The molecular rise in the boiling point was found to increase with the dilution and also with the concentration, passing, therefore, through a minimum, just as the molecular freezing point lowering of water passes through a minimum. The molecular rise not only increased with the concentration, but in the most concentrated solutions had a value almost twice that of the boiling point constant for methyl alcohol, and much larger than the boiling point constant for ethyl alcohol.

These boiling point results in the alcohols could be explained only in terms of the same theory as was applied to the freezing point results in aqueous solutions. Just as in the latter we had hydrates formed, removing a part of the water from the rôle of solvent, so here we have alcoholates, or a part of the alcohol no longer plays the rôle of solvent, but is combined with the dissolved substance.

Attention should be called here to the following facts, which, if not clearly recognized, would lead to confusion. While the complexity of the solvate in combination with any dissolved particle increases with the dilution, as would be demanded by the law of mass action, the *total amount of the solvent combined* with the dissolved substance increases with the concentration of the solution—the more concentrated the solution the smaller the amount of solvent present acting as such.

This accounts for the increase in the molecular lowering of the freezing point, and in the molecular rise in the boiling point, which have been so generally observed.

[1] This Journal, **35**, 316 (1906).

Dissolved substances, then, combine with the alcohols as they combine with water, though probably not to the same extent.

At this stage in the development of the hydrate theory Jones[1] prepared a brief statement of the evidence that had been obtained up to that time for the correctness of the theory.

Investigations in Mixed Solvents.

The investigations of Jones and his coworkers, Lindsay, Carroll, Bassett, Bingham, Rouiller, McMaster, Veazey, Mahin, and Schmidt,[2] on the conditions of dissolved substances in mixed solvents, have led to results which bear upon the theory of solvation. This work included the solvents water, methyl alcohol, ethyl alcohol, and acetone, and mixtures of each solvent with all of the others. A large number of salts have been studied in the separate solvents and also in the mixed solvents.

The conductivity of a salt like potassium iodide, in mixtures of water and methyl alcohol, for example, passed through a well-defined *minimum* in a particular mixture of the two solvents. The appearance of this minimum was satisfactorily explained by the facts brought to light by Jones and Murray,[3] in their work on the effect of one associated solvent on the association of another associated solvent with which it was mixed. It was shown by them that when two associated solvents, such as water and acetic or formic acid, are mixed, each diminishes the association of the other.

The same conclusion would apply to two such associated solvents as water and methyl alcohol. Since of two such solvents each diminishes the association of the other, each would diminish the dissociating power of the other, and, consequently, a mixture of two such solvents in the proper proportions could easily have less dissociating power than either solvent separately.

A salt dissolved in mixtures of two associated solvents would show a minimum conductivity in that particular mixture

[1] Z. physik. Chem., **55,** 385 (1906).
[2] Carnegie Publication, No. 80 (1907).
[3] THIS JOURNAL, **30,** 193 (1903).

where each solvent diminished the association of the other to a maximum extent, or where, at least, the sum of the effects was a maximum.

When, however, acetone was used as one of the solvents, this minimum did not appear, but, on the contrary, a pronounced *maximum* manifested itself in the conductivity curve, especially when the salt was lithium nitrate or calcium nitrate, and the solvent a mixture of acetone with methyl or ethyl alcohol.

It was shown[1] that this maximum may be due, theoretically, to either of two causes: either to an increase in the dissociation, increasing the number of ions present, or to a diminution in the size of the ionic spheres, which would cause the ions to move more rapidly. One of these possible factors could easily be eliminated. The direct measurement of the dissociation in mixtures of the above-named solvents showed that such mixtures do not dissociate to a greater extent than would be calculated from the dissociating power of the individual solvents. Having eliminated this factor, we must conclude that the conductivity maximum referred to above is produced by a change in the degree of solvation of the ions.

"In[2] dealing with conductivity in single solvents and in mixtures of these with one another, we must take into account the sizes of the spheres of the solvents around the ions, and any changes in the sizes of these spheres in different mixtures of the solvents.

"Any change in the size of these spheres would produce a change in the effective mass of the ion, and, consequently, a change in the velocity with which it would move.

"The size of the ionic spheres is an important factor in determining conductivity, and changes in the sizes of these spheres in different mixtures of the solvents are the prime factor in conditioning the maximum in the conductivity curve."

The bearing of solvation upon the temperature coefficients of conductivity in nonaqueous and mixed solvents is as im-

[1] Carnegie Publication, No. 80 (1907).
[2] *Ibid.*, No. 80, p. 222 (1907).

portant as the bearing of hydration upon the temperature coefficients of conductivity in aqueous solutions. In the case of nonaqueous solvents, however, a new phenomenon manifested itself, *i. e., negative temperature coefficients*.

A satisfactory explanation for this was, however, furnished.

Work of Pearce.

Jones and Pearce[1] studied a problem which was suggested by the hydrate theory. They measured the dissociation of electrolytes by both the conductivity and the freezing point methods and compared the results obtained by the two methods.

In terms of the hydrate theory, the dissociation as measured by the freezing point method should be *greater* than as measured by conductivity, and for the following reasons: If a part of the water present is not acting as solvent, but is in combination with the ions of the electrolyte, this would affect the freezing point lowering nearly proportionally, since, over small ranges in concentration freezing point lowering is nearly a linear function of the concentration.

Hydration of the ions would also affect conductivity. The greater the hydration, the greater the mass of the ion, and, consequently, for a constant driving force, the more slowly the ion would move. While the conductivity method would, therefore, not give the true dissociation of the electrolyte, it would be affected by the hydration not linearly, but to a much smaller extent. The dissociation as measured by the freezing point lowering should, therefore, be greater than as measured by the conductivity method.

The work of Pearce included calcium chloride, strontium chloride, magnesium chloride, barium chloride, calcium nitrate, strontium nitrate, magnesium nitrate, barium nitrate, cobalt chloride, cobalt nitrate, copper chloride, copper nitrate, nickel nitrate, aluminium chloride, sodium bromide, hydrochloric, nitric, and sulphuric acids.

Thus, fifteen salts and three strong acids have been brought within the scope of this investigation and the results obtained are strictly in accord with what would have been predicted

[1] This Journal, **38**, 683 (1907).

from the hydrate theory. "Since the hydration of the ion increases with increase in dilution, the volume and mass of the ionic complex is greater, the more dilute the solution; and, therefore, the greater will be the resistance to be overcome by the ion as it moves through the solvent. This being the case, the dissociation as measured by the conductivity method will be *less* than the true dissociation, and the abnormality in the dissociation measured will increase with increasing dilution.

"If we compare the values for the dissociation α, obtained, on the one hand by the conductivity method and on the other by the freezing point method, we shall see that in the case of every salt studied, without exception, the dissociation as calculated from the freezing point lowering is higher than the dissociation as calculated from the conductivity measurements."

Another point of interest, and perhaps of some importance, came out as the result of the work of Pearce.

It having been shown that the ions have such large hydrating power, the question arises as to whether the cation or the anion has the greater hydrating power. A careful study of all of the results obtained, comparing the salts with a common cation, and those with a common anion, makes it very probable that hydrating power is primarily a function of the cation.

A relation between *atomic volumes and hydrating power* was also observed. Reference to the well-known atomic volume curve will show that potassium, rubidium, and caesium have the largest atomic volumes, these elements occupying the highest maxima on the curve. Salts of these elements usually crystallize from aqueous solutions without water of crystallization, and salts of these metals have been shown by direct experiment to have very little hydrating power when in aqueous solution. Lithium and sodium also occupy maxima on the atomic volume curve, but have much smaller atomic volumes than the three elements named above. Some of the salts of lithium and sodium crystallize with two and three molecules of water.

The elements cobalt, nickel, copper, manganese, iron, and chromium fall at the third minimum in the atomic volume

curve. The salts of all of these metals crystallize with large amounts of water, and all of them show in solution great hydrating power. Aluminium with about one-half the atomic weight of iron has a somewhat greater atomic volume. It lies at the second minimum on the atomic volume curve. Its salts show great hydrating power, and crystallize from solution with as much as from six to eight molecules of water.

If now we turn to the metals of the alkaline earth group, we see that barium has the largest atomic volume, and barium chloride crystallizes with two molecules of water, while the chlorides of calcium, strontium, and magnesium crystallize with six molecules of water each. The atomic volumes of magnesium, calcium, and strontium are less than the atomic volume of barium. The magnesium cation has the smallest atomic volume of any element of this group, and has the greatest hydrating power. Calcium has a smaller atomic volume than strontium and has a greater hydrating power. Strontium has a larger atomic volume than calcium, and has a smaller hydrating power.

These relations[1] can readily be seen by consulting the curve sheets already referred to.

The above described relations seem to be sufficiently general to justify the conclusion that water of crystallization is closely connected with atomic volumes, in a number of cases—the smaller the atomic volumes the larger the amounts of water of crystallization. We have seen that there is a very close relation between water of crystallization and hydrating power. There must, therefore, be a connection between the magnitude of the atomic volumes of the cations and the hydrating power of the salts, and the relation indicated by such facts as those described above is that *the hydrating power is an inverse function of the atomic volume.*

The question then arises: Why do ions with small atomic volumes have greater power to combine with water, than atoms with larger atomic volumes? It is probably connected in some way with the electrical density of the charge upon the ions—the smaller the ionic volume the greater would be

[1] J. Chim. Phys., **3,** 455 (1905).

the density of the charge upon it. The effect of hydration upon the velocities of the ions was also pointed out by Jones and Pearce.[1] The velocities of the ions are a function of their mass, and perhaps of their volumes. If there were no hydration of the ions, we should, then, expect those ions with the smallest mass and smallest atomic volumes to have the greatest velocities, under a constant driving force.

We find that, with the exception of hydrogen and hydroxyl, the elements with the largest atomic volumes—potassium, rubidium, and caesium move with the greatest velocities, while the ions of the iron and copper groups, with somewhat greater masses, but with very small atomic volumes, have small migration velocities.

We have just seen that it is the cations with the smallest atomic volumes that have the greatest hydrating power. The increased mass of these ions, due to the hydrates which they carry with them, therefore causes them to move more slowly than ions with much larger atomic volumes. The existence of hydrates accounts, then, for the apparent lack of any relation between ionic velocities and the mass and size of the ions. If we take into account the hydration the apparent discrepancy disappears.

Work of Stine.

Jones and Stine[2] studied the effect of one salt with hydrating power upon the hydration of another salt present in the same solution. The pairs of salts with which they worked are: calcium chloride and potassium chloride; calcium chloride and magnesium chloride; calcium chloride and strontium chloride; magnesium nitrate and strontium nitrate; magnesium nitrate and calcium nitrate; aluminium chloride and ferric chloride; calcium nitrate and calcium chloride; sodium bromide and lithium bromide; and, finally, potassium chloride and ammonium chloride, which have practically no hydrating power.

The problem resolved itself into calculating the approximate composition of the hydrates formed by both of the sub-

[1] This Journal, **38**, 737 (1907).
Ibid., **39**, 313 (1908).

stances present in the solution, and, as can be seen at a glance, was a difficult one. Indeed, the difficulties involved in calculating the approximate composition of the hydrates formed by one substance in the presence of water were multiplied many times when two substances were present.

However, by taking into account as closely as possible all of the factors involved—and they are many—we were able to throw considerable light on the problem. The effect of a salt with a common ion on the conductivity of a second salt was apportioned in terms of the law of mass action. The formula was worked out for calculating the freezing point lowering due to hydration when only one salt has hydrating power, and, similarly, the corresponding formula when both salts form hydrates.

It will be recognized that in the pairs of salts selected above we have a large variety of conditions represented. The first two have a common anion and only one has any appreciable hydrating power. Further, one salt is a binary and the other a ternary electrolyte. The next four pairs are ternary electrolytes, having a common anion, and both members of each pair have large hydrating power. The next two are quaternary electrolytes with a common anion and both have large hydrating power. The next two have a common cation. The pair next to the last have a common anion, and both members show considerable hydrating power, while the last pair have a common anion and neither member has any appreciable hydrating power.

It was found that when two hydrated salts are mixed each dehydrates the other to a certain extent, and that the magnitude of this action is conditioned by the law of mass action, which could be the case only if the composition of the hydrates as worked out was approximately correct.

It was further shown that the ions and the molecules have very different hydrating power, and that while, in general, the ions have the greater power to form hydrates, in some special cases the molecules have a greater power than the ions to combine with water.

Some interesting results were obtained with the pair of

electrolytes, potassium chloride and ammonium chloride, which have but little hydrating power. When two salts having a common ion are mixed, each drives back the conductivity of the other, and it has been thought that this is due almost entirely to each suppressing the dissociation of the other. If this were the sole explanation, then we should have the greatest effect on the conductivity under the conditions under which the salts in question were most dissociated.

Since the dissociation is greater at $0°$ than at $25°$, for example, the effect on the conductivity ought to be greater at the former than at the latter temperature.

The fact is exactly the reverse.[1] There is very little driving back of the conductivity at $0°$, considerable effect at $12°$, and a very pronounced difference between the conductivity of the mixed salts and the sum of the separate conductivities at $25°$.

It is thus obvious that the suppression of the ionization is not the only factor that must be taken into account here. This is especially true since a number of the solutions referred to above are practically isohydric.

The other factors that must be taken into account are:

(1) Change in viscosity of the solution on mixing the two salts.

(2) Change in the size and mass of the ionic spheres, due to a change in the hydration when the two salts are mixed.

"Thus, the effect of one salt upon another present in the same solution is not as simple as has been supposed but involves the action of several factors which have to be taken into account."

Work of Jacobson.

The work of West on the temperature coefficients of conductivity and of dissociation was continued by Jacobson.[2] He improved the method that had been earlier used, and extended the investigation to lithium chloride, lithium bromide, lithium nitrate, lithium sulphate, sodium nitrate, disodium phosphate, potassium sulphocyanate, potassium chromate,

[1] This Journal, **39**, 399 (1908).

[2] *Ibid.*, **40**, 355 (1908).

potassium dichromate, calcium nitrate, strontium chloride, strontium nitrate, strontium formate, barium bromide, barium nitrate, barium formate, barium acetate, magnesium sulphate, cupric bromide, chromium chloride, chromium nitrate, ferric chloride, ferric nitrate, nickel sulphate, nickel acetate, cobalt sulphate, cobalt acetate, lead nitrate, trichloracetic acid, racemic acid, picric acid, propionic acid, *o*-nitrobenzoic acid, and *m*-nitrobenzoic acid.

It will be seen that the compounds were so chosen as to cover as wide a range of physical and chemical properties as possible.

The increase in the conductivity of electrolytes with rise in temperature is largely due to the fact that the ions in the presence of water are hydrated. With rise in temperature the magnitude of the hydration becomes less and less, and the mass of the ions and probably their size become less. They would, consequently, move through the solvent with greater velocity and the conductivity would increase.

Those ions that are hydrated to the greatest extent would then be most affected by rise in temperature. An examination of the experimentally established facts will show that they are in accord with this conclusion.

It was shown that the conductivity of electrolytes increases with rise in temperature, *not as a linear function, but as a parabolic one*. Water, however, is an exception. Its conductivity increases with rise in temperature, as a linear function of the temperature. This is probably due to the fact that the hydrogen and hydroxyl ions from the dissociated water are not appreciably hydrated, and there is, therefore, no marked change in the hydration with rise in temperature The increase in the conductivity of water with rise in tem perature is due chiefly to the diminishing viscosity of this solvent as the temperature is raised. The change in the viscosity with rise in temperature is known to be a linear function of the temperature. Therefore, we should expect the temperature coefficient in the case of a substance like water to be a linear function of the temperature. Jacobson calls attention to the importance of hydrolytic dissociation

as affecting conductivity, and points out that many of the apparently abnormal results that have been obtained are due to this cause.

His investigation confirms, in general, the conclusions drawn by Jones from the work of West, and is, therefore, in perfect accord with the hydrate theory.

Spectroscopic Investigation of Jones and Uhler.

The spectroscopic investigation, which is the outcome of certain color changes in solution to which Dr. G. N. Lewis kindly called my attention, had for its object the study of the rôle played by hydration as conditioning certain color changes in solution with change in concentration and on the addition of a second salt. Thus, the change in the color of aqueous solutions of copper salts with change in the dilution is very well known. Further, the purplish-red color of aqueous solutions of cobalt chloride is changed to blue on the addition of a concentrated solution of calcium chloride.

"In[1] the present investigation these color changes were studied quantitatively. The absorption spectra of the substances separately, and when mixed in known quantities, have been observed by means of a direct reading spectroscope, and the wave lengths of the absorption bands read off and recorded. What is of far greater importance, however, is the photographic record of such absorption bands, and the changes in the positions of these bands as varying amounts of one or another dehydrating agent is added to the salt in question,"

A grating spectrograph was used for securing the photographic records, and a direct vision spectroscope for the eye observations. The solutions were placed in cells with quartz ends to allow of work also in the ultraviolet region. A spark rich in ultraviolet light was employed and the Nernst filament was also used. The films employed were Seeds' L-ortho cut films.

The substances studied at different concentrations in water were: cobalt chloride, cupric chloride, and cupric bromide.

[1] Carnegie Publication, No. 60, p. 161 (1907).

It was found that the absorption bands widen for every salt with increase in the concentration of the solution. This leads us to say a word as to what is meant by absorption of light by dissolved substances.

In order that a substance in solution should stop a beam of light it must yield or form something in the solution that is thrown into resonance by the light. If it absorbs only certain wave lengths of light, as in the case of colored solutions, the dissolved substance must yield "absorbers" which can be thrown into resonance by those wave lengths of light which are stopped by the substance. Light waves are vibrations in the ether. In order that they may be stopped, their energy must be expended in some manner, as in throwing electrons into vibration. Absorption of light, then, means resonance.

With this idea in mind we can proceed to interpret the results obtained by Jones and Uhler.

The absorption bands widen with increase in the concentration of the solution. A widening of the absorption bands means that there is something in the solution which vibrates in resonance with a larger number of wave lengths of light. What absorber could there be in a more concentrated solution of cobalt chloride that would vibrate in resonance with a larger number of wave lengths of light than in a more dilute solution?

Jones and Uhler interpret this result as follows: We know that the hydrate present in the more concentrated solution is simpler than in the more dilute. The vibrating particle or "absorber" is, then, less loaded down and hampered in its vibrations in the more concentrated solution, and can, therefore, vibrate in resonance with a larger number of wave lengths of light. A larger number of wave lengths are accordingly cut out in the more concentrated solution and the absorption bands widen.

Jones and Uhler studied not only the effect of increasing the concentration of the solution of a single substance on its power to absorb light, but also the effect of adding a dehydrating agent in the form of a second salt to the solution of the colored salt. Thus, calcium chloride was added to

cobalt chloride, calcium bromide to cobalt chloride, aluminium chloride to cobalt chloride, calcium chloride to copper chloride, calcium bromide to copper chloride, aluminium chloride to copper chloride, calcium chloride to copper bromide, calcium bromide to copper bromide, and aluminium chloride to copper bromide.

The effect of the addition of the dehydrating agent in the form of a second salt is to *widen the absorption band.* It, therefore, produces the same effect as increasing the concentration of the colored salt alone, and can readily be explained in the same manner. The dehydrating agent removes a part of the water from the colored salt—makes the hydrate less complex. The vibrating particles, or "absorbers," are freer to vibrate in resonance with a larger number of wave lengths of light, since they are surrounded by a smaller atmosphere of the solvent. Their freer vibration enables them to cut out a larger number of light waves and, consequently, to widen the absorption bands.

The hydrate theory accounts, then, satisfactorily for the widening of the bands produced by increasing the concentration of the solution, and also by adding a second salt with a large hydrating power.

Further, it was pointed out by Jones and Uhler[1] that this is the only theory thus far proposed that does account satisfactorily for all of the facts brought out by them.

The theory of Engel, that the blue color of solutions of cobalt chloride is due to the presence of double salts, is untenable for a number of reasons. Jones and his coworkers have shown that double salts do not exist in solution to any very great extent. Further, this theory is at variance with the fact that a concentrated aqueous solution becomes blue on heating, and also with the facts established in nonaqueous solutions.

The theory of Ostwald, which would refer the blue color to the cobalt salt molecule, and the red color to the cobalt ion, is insufficient. It cannot account satisfactorily for the blue color produced on warming a concentrated aqueous

[1] Carnegie Publication, No. 60, p. 232 (1907).

solution of cobalt chloride. The dissociation would change only slightly, and hydrolysis would not liberate sufficient hydrochloric acid to drive back the dissociation appreciably.

It does not account for the fact that a very small amount of water changes to red a solution of cobalt chloride rendered blue by aluminium chloride. It fails to account for the fact that the amount of water required to turn red a blue alcoholic solution of anhydrous cobalt chloride is many times too small to produce an increased dissociation sufficient to give the observed color change.

Further, this theory is entirely incapable of explaining results obtained by Jones and Anderson[1] in their recent work on absorption in solution, and which will soon be published in full by the Carnegie Institution, of Washington, and in part in THIS JOURNAL. This work has shown that when the number of molecules in the path of the beam of light is kept constant, certain absorption bands, such as the ultraviolet absorption of copper, the red bands of cobalt salts, the ultraviolet band of cobalt chloride, and the absorption of iron chloride, *narrow with the dilution*, and there are still other facts known which the Ostwald theory cannot explain.

The theory of Dannan and Bassett, that the blue color of cobalt salts is due to complex ions of cobalt, is also insufficient. For example, it has been shown by Hartley and others that the effect on the absorption of increasing the concentration of the solution is essentially the same as that produced by a rise in temperature.

This is strong evidence against the theory of aggregates or complex ions as accounting for the color changes, since the change in the aggregates produced by *increase in concentration* is exactly the *opposite* of that produced by *rise in temperature*. It is obvious that the theory of solvation to account for the color changes is not open to this objection, since it is well known that rise in temperature produces the *same* effect on solvates as increase in concentration. The solvates become simpler with increase in concentration, and also with rise in temperature.

[1] Carnegie Publication, No. 110 (1909).

All of the facts brought out by Jones and Uhler, and also those established by Jones and Anderson, working in aqueous solutions, can be accounted for satisfactorily in terms of the hydrate theory and in terms of this alone. It now remains to see whether the facts established in nonaqueous solutions can also be accounted for in terms of the theory of solvation.

The work of Jones and Uhler was extended to solutions in nonaqueous solvents, such as methyl alcohol, ethyl alcohol, and acetone, and the salts investigated were: cobalt chloride in methyl alcohol, cobalt chloride in ethyl alcohol, cobalt chloride in acetone, copper chloride in methyl alcohol, copper chloride in ethyl alcohol, copper chloride in acetone, copper bromide in methyl alcohol, and copper bromide in ethyl alcohol. For work with these solutions in nonaqueous solvents a form of cell was devised which did away entirely with all forms of cement, since no cement could be found which would resist entirely the action of all of these solvents. The cell used by Jones and Uhler[1] worked perfectly satisfactorily.

To these nonaqueous solutions varying amounts of water were added, and the effect on the absorption bands recorded by means of photographs. The effect of the addition of water was, in every case, to *narrow the absorption band.* This is regarded as an important fact as bearing upon the hydrate theory. As more and more water was added the hydrates formed became more and more complex. The "absorbers" were, thus, more and more limited in their resonance, by the larger and larger hydrate around them, and could vibrate in resonance only with a smaller number of wave lengths of light. Consequently, the absorption bands became narrower and narrower as the amount of water present increased.

Work of Jones and Anderson on the Absorption Spectra of Solutions.

The work of Jones and Anderson, on absorption spectra in nonaqueous solutions, also established a number of facts

[1] Carnegie Publication, No. 60, p. 242 (1907).

which are of importance as bearing on the hydrate theory. This is especially true in the case of neodymium chloride in methyl alcohol, for example, and in mixtures of methyl alcohol and water. When the amount of water present is only a few per cent, we have *two distinct spectra*, one corresponding to the aqueous solution, and the other to the nonaqueous solution. These two spectra appear simultaneously, the one or the other being more intense depending upon the relative amounts of water and the alcohol present. This seems to be the first time that such an observation has been made. A number of other points bearing upon the hydrate theory were brought out in the work of Jones and Anderson, but as a pretty full account of this work will soon be published in THIS JOURNAL, no further details will be given here.

To summarize, then, the evidence that has been obtained thus far, as bearing upon the solvate theory, we have:

(1) The relation between water of crystallization and lowering of the freezing point, holding for such a large number of substances, is regarded as strong evidence for the existence of complex hydrates in aqueous solutions.

(2) The fact that the minimum in the boiling point curve for a given substance occurs at a greater concentration than the minimum in its freezing point curve is just what would have been predicted from the solvate theory.

(3) The relation between water of crystallization and temperature of crystallization—the lower the temperature the larger the amount of water of crystallization—is strictly in accord with what would be expected from the solvate theory.

(4) The connection between the hydrating power of the ions and the temperature coefficients of conductivity is a strong argument in favor of the solvate theory. Those ions with the greatest hydrating power have the largest temperature coefficients, as we would expect; and the more dilute solutions containing more complex hydrates have larger temperature coefficients than the more concentrated.

(5) The evidence for the existence of solvates in nonaqueous

solvents is of the same general character as that for the existence of hydrates in aqueous solutions.

(6) The existence of a pronounced conductivity maximum in certain mixed solvents shows that the ions are surrounded by an atmosphere of the solvent, which changes in magnitude with change in the composition of the mixture.

(7) The fact that dissociation as measured by the freezing point method is greater than as measured by conductivity was predicted from the solvate theory before a single comparative measurement was made. It was also shown in this work that the smaller ions have the greater hydrating power.

(8) The effect of one salt with hydrating power upon another salt present in the same solution, also having hydrating power, was predicted by the hydrate theory, and is in conformity with the law of mass action.

(9) The evidence for the solvate theory, from the study of the absorption spectra of aqueous solutions, is certainly most striking. The absorption bands widen with the concentration, due to the hydrate becoming simpler, and the "absorbers" being freer to vibrate. They also widen with the addition of a dehydrating agent, and for the same reason.

(10) The absorption spectra in nonaqueous solutions to which more and more water is added furnish evidence, which is equally strong, for the existence of hydrates. With addition of water to the nonaqueous solution its absorption bands grow narrower, due to the hydrates around the absorbers becoming more and more complex.

Further spectroscopic evidence for the existence of hydrates in aqueous solutions, and of solvates in solution in general, will be furnished when the work of Jones and Anderson, and also that of Jones and Strong, are published.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
October, 1908.

CLXV.—RESEARCHES ON PYRIMIDINES:
ON THE FORMATION OF PURINE DERIVATIVES FROM
4-METHYLCYTOSINE.

[FORTY-FIRST PAPER.]

By Carl O. Johns.

It was found by Gabriel and Colman that 4-methyl-6-aminopyrimidine[1] and 2-chlor-4-methyl-6-aminopyrimidine[2] did not give the expected 5-nitro compounds when nitrated, but instead yielded 6-nitramine derivatives.

When 4-methylcytosine, I.,[3] is nitrated in the presence of sulphuric acid, an almost quantitative yield of 4-methyl-5-nitrocytosine, II., is obtained. To determine whether the compound formed was a 6-nitramine or a 5-nitropyrimidine, the nitration product was heated with 30 per cent sulphuric acid in a sealed tube. This treatment gave Behrend's nitromethyluracil,[4] III., in which the nitro group occupies position 5. This result agrees with previous observations made when pyrimidines containing an amino group in position 6 have been heated with sulphuric acid. When cytosine[5] was heated with 20 per cent sulphuric acid it gave uracil, and when nitrocytosine[6] was heated under similar conditions, nitrouracil was formed.

The reduction of 4-methyl-5-nitrocytosine to 2-oxy-4-methyl-5,6-diaminopyrimidine, IV., presented considerable difficulty. This was not unexpected since it was only after many unsuccessful attempts that 2-oxy-5,6-diaminopyrimidine[7] was obtained by the reduction of 5-nitrocytosine.

An attempt to reduce 4-methyl-5-nitrocytosine with stannous chloride did not give the desired diaminopyrimidine, and when ammonium sulphide was used, 4-methylcytosine

[1] Ber. d. chem. Ges., **34**, 1240 (1901).

[2] *Ibid.*, **34**, 1241 (1901).

[3] This Journal, **40**, 348 (1908).

[4] Ann. Chem. (Liebig), **240**, 3 (1887).

[5] Wheeler and Johnson: This Journal, **29**, 494 (1903).

[6] Johnson, Johns, and Heyl: *Ibid.*, **36**, 116 (1906).

[7] *Ibid.*, **36**, 170 (1906).

was regenerated. The reduction was finally accomplished by the use of aluminium amalgam. Even then prolonged reduction or a temperature above 45° liberated ammonia and regenerated 4-methylcytosine. If the solution which was obtained from the reduction was evaporated on a water bath at 100° a black residue was obtained. The evaporation was therefore carried out under diminished pressure. When the solution had been concentrated to a small volume, stout, flat crystals of the 2-oxy-4-methyl-5,6-diaminopyrimidine separated. These contained one and one-half molecules of water of crystallization. They could be recrystallized from water without undergoing decomposition and then separated in long prisms that contained but one molecule of water. It is probable that the decomposition observed when the solution obtained from the reduction was evaporated was due to the presence of some unstable by-product.

Gabriel and Colman condensed urea[1] and thiourea[2] with 4-methyl-5,6-diaminopyrimidine and obtained purine derivatives.

The writer has found that 2-oxy-4-methyl-5,6-diaminopyrimidine also condenses with urea and thiourea to give 2,8-dioxy-6-methylpurine, V., and 2-oxy-6-methyl-8-thiopurine, VI. Moreover, formic acid acts on 2-oxy-4-methyl-5,6-diaminopyrimidine and produces a monoformyl derivative. This compound gives a sodium salt which loses water, when heated, and yields 2-oxy-6-methylpurine, VII.

These reactions with urea and formic acid are such as might be expected of an orthodiamine but not of a hydrazine derivative, and they confirm the assumption that 4-methylcytosine nitrates in position 5.

Emil Fischer[3] has called attention to the fact that the introduction of oxygen into purine decreases its solubility in water. In accordance with this, 2-oxy-6-methylpurine is easily soluble in hot water while the same purine with oxygen or sulphur in position 8 is almost insoluble.
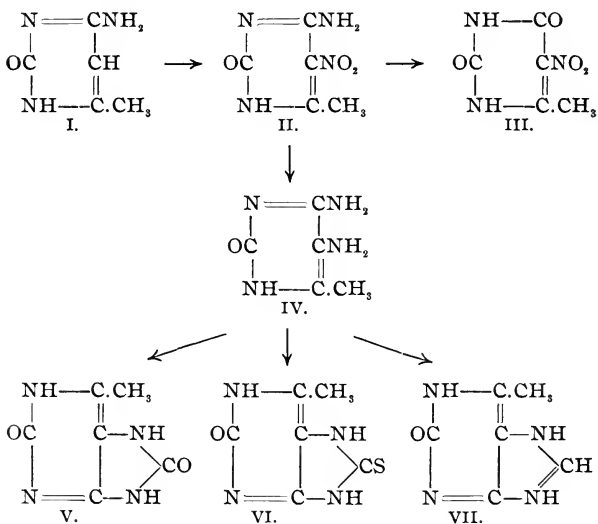
If 2-oxy-5,6-diaminopyrimidine were heated with urea it

[1] Ber. d. chem. Ges., **34,** 1247 (1901).
[2] *Ibid.*, **34,** 1248 (1901).
[3] Untersuchungen in der Puringruppe, p. 74.

might be expected to yield 2,8-dioxypurine. This compound is the only one of the three possible dioxypurines which has not been prepared and it has the structure which was at first assigned to xanthine. Later, Emil Fischer showed that xanthine was 2,6-dioxypurine.[1] 6,8-Dioxypurine has been prepared by Fischer and Ach.[2] The writer has begun work on the synthesis of 2,8-dioxypurine.

$$
\begin{array}{ccc}
\text{N}\!=\!\!=\!\!\text{CNH}_2 & \text{N}\!=\!\!=\!\!\text{CNH}_2 & \text{NH}\!-\!\!-\text{CO} \\
| \quad\quad | & | \quad\quad | & | \quad\quad | \\
\text{OC} \quad \text{CH} & \text{OC} \quad \text{CNO}_2 & \text{OC} \quad \text{CNO}_2 \\
| \quad\quad \| & | \quad\quad \| & | \quad\quad \| \\
\text{NH}\!-\!\!-\text{C.CH}_3 & \text{NH}\!-\!\!-\text{C.CH}_3 & \text{NH}\!-\!\!-\text{C.CH}_3 \\
\text{I.} & \text{II.} & \text{III.}
\end{array}
$$

$$
\begin{array}{c}
\text{N}\!=\!\!=\!\!\text{CNH}_2 \\
| \quad\quad | \\
\text{OC} \quad \text{CNH}_2 \\
| \quad\quad \| \\
\text{NH}\!-\!\!-\text{C.CH}_3 \\
\text{IV.}
\end{array}
$$

$$
\begin{array}{ccc}
\text{NH}\!-\!\!-\text{C.CH}_3 & \text{NH}\!-\!\!-\text{C.CH}_3 & \text{NH}\!-\!\!-\text{C.CH}_3 \\
| \quad\quad \| & | \quad\quad \| & | \quad\quad \| \\
\text{OC} \quad \text{C}\!-\!\text{NH} & \text{OC} \quad \text{C}\!-\!\text{NH} & \text{OC} \quad \text{C}\!-\!\text{NH} \\
| \quad\quad\quad \rangle\text{CO} & | \quad\quad\quad \rangle\text{CS} & | \quad\quad\quad \rangle\text{CH} \\
\text{N}\!=\!\!=\!\!\text{C}\!-\!\text{NH} & \text{N}\!=\!\!=\!\!\text{C}\!-\!\text{NH} & \text{N}\!=\!\!=\!\!\text{C}\!-\!\text{NH} \\
\text{V.} & \text{VI.} & \text{VII.}
\end{array}
$$

Experimental Part.

4-Methyl-5-nitrocytosine,
$$
\begin{array}{c}
\text{N}\!=\!\!=\!\!\text{CNH}_2 \\
| \quad\quad | \\
\text{OC} \quad \text{CNO}_2. \\
| \quad\quad \| \\
\text{NH}\!-\!\!-\text{C.CH}_3
\end{array}
$$
—Four grams of 4-

methylcytosine were dissolved in 11 cc. of concentrated sulphuric acid. Heat was liberated. While the solution was still

[1] Ber. d. chem. Ges., **30,** 553 (1897).
[2] *Ibid.*, **30,** 2218 (1897).

warm 11 cc. of nitric acid, density 1.5, were added gradually. The first portions of nitric acid produced considerable heat but no red fumes were evolved. The resulting solution was allowed to stand at room temperature for 10 minutes and was then poured into 100 cc. of cold water. When the acids were neutralized with ammonium hydroxide, 4.8 grams of a yellow precipitate, which corresponds to 90 per cent of the calculated yield, separated. This compound was difficultly soluble in boiling water and crystallized in small pointed prisms. Its slight solubility in water showed that it was not 4-methyl-cytosine. It began to turn brown at 260° and became black at 280° but did not melt. It was soluble in acids and ammonia.

Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_4$.	Found.
N	32.94	33.17

The position of the nitro group was determined as follows: One gram of the nitro compound was dissolved in 20 cc. of 30 per cent sulphuric acid and heated in a sealed tube at 130°–140° for two hours. A deposit of large crystals was obtained when the tube cooled. These were filtered off and the filtrate was analyzed for nitrogen in the form of ammonia by adding sodium hydroxide and distilling into N/10 hydrochloric acid.

N calculated for one NH_2 group, 0.08 gram.

Found, 0.09 gram.

The crystals which were filtered off dissolved readily in boiling water and separated from the cold solution in stout prisms and toothed structures. They possessed all the properties of Behrend's nitromethyluracil, in which the nitro group occupies position 5.

	Calculated for $C_5H_6O_4N_3$.	Found.
N	24.56	24.99

2-Oxy-4-methyl-5,6-diaminopyrimidine,
$$\begin{array}{c} N = CNH_2 \\ | \qquad | \\ OC \qquad CNH_2 \\ | \qquad || \\ NH - C.CH_3 \end{array}$$
—Two
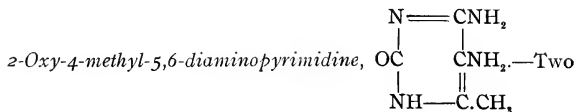
and two-tenths grams of finely pulverized 4-methyl-5-nitro-

cytosine were suspended in 100 cc. of water and reduced vigorously with 1 gram of aluminium amalgam for one-half hour. The temperature was kept below 45°. The aluminium used was in the form of fine drillings. The aluminium hydroxide formed was filtered off by suction and washed with hot water. The filtrate was concentrated under diminished pressure to about 15 cc. Crystals separated during the evaporation. These were redissolved by careful heating and a slight insoluble residue was filtered off. Stout, flat prisms separated on cooling. These became brown above 250° and decomposed slowly at about 280°–285° without melting. They contained one and one-half molecules of water of crystallization. The yield of pure hydrous crystals was from 50 to 60 per cent of the calculated. Water determinations on crystals obtained from different experiments gave the following results:

I. 1.6340 gram lost 0.2637 gram of H_2O.

II. 0.5011 gram lost 0.0805 gram of H_2O.

III. 1.1859 gram lost 0.1907 gram of H_2O.

	Calculated for $C_5H_8ON_4.1\frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	16.16	16.14	16.06	16.08

Nitrogen determinations resulted as follows:

	Calculated for $C_5H_8ON_4.1\frac{1}{2}H_2O$.	Found.
N	33.53	33.61

	Calculated for $C_5H_8ON_4$.	Found.
N	40.00	39.78

When the flat crystals obtained above were recrystallized from water they separated in long prisms that contained but one molecule of water of crystallization. The following analyses were made on different lots of the recrystallized diaminopyrimidine.
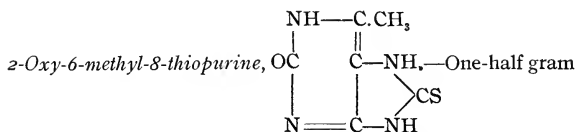
	Calculated for $C_5H_8ON_4.H_2O$.	I.	Found. II.	III.
H_2O	11.39	11.53	11.49	11.42

	Calculated for $C_5H_8ON_4$.	Found.
N	40.00	40.02

2-Oxy-4-methyl-5,6-diaminopyrimidine was easily soluble in hot water but it dissolved only slightly in cold water. It did not dissolve in alcohol. The dried crystals were very hygroscopic. Water solutions gave precipitates with mercuric chloride and picric acid. The picrate charred above 240° but did not melt. The best yield was obtained by using fine aluminium drillings and reducing rapidly. If the reduction is prolonged or the temperature raised above 45°, ammonia is liberated and 4-methylcytosine is re-formed.

2,8-Dioxy-6-methylpurine,

$$\begin{array}{c}\text{NH}\!-\!\!-\!\!\text{C.CH}_3 \\ | \quad\quad \| \\ \text{OC} \quad\quad \text{C}\!-\!\text{NH.} \\ | \quad\quad | \quad\quad \!\!>\!\!\text{CO} \\ \text{N}\!=\!\!=\!\!\text{C}\!-\!\text{NH} \end{array}$$
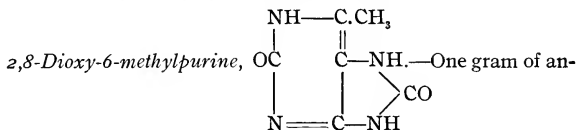
—One gram of anhydrous 2-oxy-4-methyl-5,6-diaminopyrimidine was intimately mixed with 1 gram of urea by grinding in a mortar. This mixture was heated in an oil bath kept at 170°–180° for one-half hour. The mass melted and ammonia was evolved. The fusion product was dissolved in boiling water containing a few drops of ammonium hydroxide and the solution was decolorized with animal charcoal. When the filtrate was boiled to drive off ammonia, minute crystals separated. These were almost insoluble in boiling water but dissolved readily in mineral acids and bases. They were insoluble in alcohol or acetic acid. They did not melt at 345°. The yield was 1.1 grams, or 93 per cent of the calculated weight.

	Calculated for $C_6H_6O_2N_4$.	I.	Found. II.
N	33.73	33.59	33.81

2-Oxy-6-methyl-8-thiopurine,

$$\begin{array}{c}\text{NH}\!-\!\!-\!\!\text{C.CH}_3 \\ | \quad\quad \| \\ \text{OC} \quad\quad \text{C}\!-\!\text{NH.} \\ | \quad\quad | \quad\quad \!\!>\!\!\text{CS} \\ \text{N}\!=\!\!=\!\!\text{C}\!-\!\text{NH} \end{array}$$

—One-half gram of 2-oxy-4-methyl-5,6-diaminopyrimidine was ground in a mortar with one gram of thiourea. The mixture was heated in an oil bath kept at 180°–190° for one hour. It melted and

turned black. Ammonia was evolved. The fusion mass was dissolved in water containing ammonium hydroxide. A clear solution was obtained by using animal charcoal. This solution gave an immediate precipitate when acidified with acetic acid. The compound thus obtained was purified by dissolving in very dilute ammonium hydroxide and reprecipitating with acetic acid. Extremely small crystals were obtained. These were not soluble in alcohol and were almost insoluble in boiling water and boiling acetic acid. They were freely soluble in alkalies and mineral acids. They did not melt at 345°. The yield of the pure purine was 80 per cent of the calculated quantity.

	Calculated for $C_5H_6ON_4S$.	Found.
N	30.77	30.90
S	17.59	17.81

The Monoformyl Derivative of 2-Oxy-4-methyl-5,6-diaminopyrimidine, $C_5H_7ON_4.CHO$.—Four grams of the diaminopyrimidine were dissolved in 4 cc. of formic acid, density 1.2, and the solution was heated on a water bath for one-half hour. The excess of formic acid was evaporated in an open dish and the residue was dissolved in water. When this solution was neutralized with ammonium hydroxide, the monoformyl derivative precipitated. It was moderately soluble in hot water and formed minute crystals when the solution was cooled. It dissolved readily in acetic acid and was slightly soluble in boiling alcohol. The crystals began to turn black at about 325° but did not melt at 345°.

	Calculated for $C_6H_8O_2N_4$	Found.
N	33.33	33.29

Prolonged heating in an oil bath at 240° caused the formyl derivative to darken considerably but it did not lose water to form a purine. When recrystallized from water the heated product exhibited all the properties of the formyl derivative. It was dried at 130° for analysis.

	Calculated for $C_6H_8O_2N_4$.	Found.
N	33.33	33.46

$$
\begin{array}{ccc}
\text{NH} & \!\!\!\!-\!\!\!\!- & \text{C.CH}_3 \\
| & & \| \\
\textit{2-Oxy-6-methylpurine,}\quad \text{OC} & & \text{C}-\text{NH} \\
| & & \qquad\diagdown\!\!\!\!\diagup\text{CH} \\
\text{N} & \!\!=\!\!= & \text{C}-\text{N}
\end{array}
\;\text{—Three grams of the}
$$
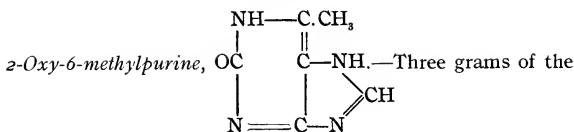
monoformyl derivative of 2-oxy-4-methyl-5,6-diaminopyrimidine were dissolved in an excess of 10 per cent solution of sodium hydroxide. When alcohol was added the sodium salt of the formylpyrimidine separated as a white powder. This salt was dried and heated in an oil bath at 200°. Water came off readily and considerable foaming ensued, leaving a porous crust. This dissolved freely in cold water and did not give a precipitate when the solution was neutralized with acetic acid. The solution was therefore evaporated to dryness and the residue was dissolved in a little hot water. Clusters of slender prisms were obtained when the solution cooled slowly. These turned brown at about 280° and became black above 300° but did not melt at 345°. They were easily soluble in acetic acid and ammonium hydroxide and sparingly soluble in boiling alcohol. A water solution gave a precipitate with mercuric chloride but did not give precipitates with ferric chloride, copper sulphate, or chloroplatinic acid.

	Calculated for $C_6H_6ON_4$.	I.	Found. II.	III.
N	37.33	37.05	37.10	37.35

NEW HAVEN, CONN.,
November, 1908.

OBITUARY.

WOLCOTT GIBBS.

Probably the oldest and certainly one of the most distinguished chemists of the United States died December 9th at his home, Newport, R. I., Wolcott Gibbs was born in New York City, February 21, 1822. He received his early education at the grammar school attached to Columbia College, and then graduated from the college in 1841. He evidently had a bent towards chemistry in his early life, for after graduating from college he spent a few months in the laboratory of Dr. Robert Hare, in Philadelphia. He then returned to New

York and studied medicine, receiving the degree of doctor of medicine from the College of Physicians and Surgeons in 1845. He spent a year and a half working in the laboratories of Rammelsberg and Heinrich Rose in Berlin. He was for some time at Giessen under Liebig, and then attended Regnault's lectures on physics at the College of France. On returning to the United States, in 1848, he gave a short course of lectures at Delaware College. From 1849 to 1863 he was professor of physics and chemistry at the College of the City of New York, when he was elected to the Rumford professorship in Harvard College and was placed in charge of the laboratory of the Lawrence Scientific School. This position he held for 24 years. Since then he has been professor emeritus, living at Newport, R. I.

He was one of the original members of the National Academy of Sciences, and from 1885 to 1891 was its president. He was a foreign member of the London Chemical Society and an honorary member of the German Chemical Society.

Most of his original work has appeared in the "Contributions to Chemistry from the Lawrence Scientific School," and he has published elaborate memoirs on the platinum metals, on the ammonia-cobalt bases, on new analytical methods, and on complex inorganic acids, discovering platinotungstates, vanadio-tungstates, vanadio-molybdates, etc. In physics he has published papers on wave lengths of light, on vapor densities, improved methods of gas analysis, and on the theory of the dynamo. Of recent years his articles have appeared chiefly in the *American Journal of Science* and in THIS JOURNAL.

Throughout his long life Dr. Gibbs was true to the highest scientific ideals and his influence on scientific research in this country was most beneficial. When he began his work he was almost alone so far as chemistry is concerned. It was a great pleasure to him that as time went on the number of those who devoted themselves to research increased more and more. His interest in all advances was great and did not diminish until within a few years. Long after he had passed his seventieth birthday he planned new researches and showed almost youthful enthusiasm on learning of some brilliant discovery.

REPORTS.

Owing to the confusion existing in the minds of many from a lack of understanding of the great number of experimental facts and theories regarding the origin of petroleum which have accumulated during the past twenty years, it is necessary in discussing this subject to consider its historical development. In addition to the cosmic theory, according to which the oil has condensed upon our planet from interplanatory space, there are the two important theories, known as the inorganic and organic, which have been suggested to explain the origin of the oil. The father of the inorganic theory is A. von Humboldt. This investigator concluded, on the basis of the proximity of certain hot springs and oil wells in South America, that the oil was the product of a destructive distillation of the older rocks. Berthelot, in 1866, was the first to offer a chemical explanation of its formation. According to this author the alkali metals and carbon dioxide reacted, forming metallic acetylides which, in turn, acting with water vapor at high temperatures, formed acetylene and oil. In 1877 Mendeléeff, and at about the same time Cloez, explained its formation as due to the action of water on hot metallic carbides in the interior of the earth. Moissan accepted this theory, as did also, on the basis of their classical work on this subject, Sabatier, and his coworkers, Senderens and Mailhe. Sabatier and Senderens established the following facts:

(1) When acetylene and an excess of hydrogen are passed over nickel, cobalt, or iron at moderate temperatures, methane and an oillike substance, consisting mainly of marsh gas hydrocarbons, resembling in general properties the Pennsylvania petroleum, is obtained.

(2) When the same action takes place at 200° the hydrocarbons first formed combine with more hydrogen and form an oil resembling the Caucassian oil and containing marsh gas hydrocarbons and naphthenes.

(3) If the product obtained in (1) is passed, with an excess of hydrogen, over nickel at 300°, an oil resembling the Galician oil, containing unsaturated cyclic hydrocarbons, is formed.

(4) By the action of nickel on a mixture of acetylene and

an insufficient supply of hydrogen an oil is obtained which stands between the Pennsylvania and Caucassian oils.

From these results the following conclusions were drawn regarding the formation of oil:

Water acting upon the free metals and carbides gives hydrogen and acetylene, and these gases, in contact with nickel or other metals, condense to form petroleum, the variety depending upon the conditions under which the condensation takes place. This inorganic theory of the origin of petroleum is, however, not tenable because it cannot give a satisfactory explanation of the presence of nitrogenous bases and especially because most natural petroleum shows optical activity, a phenomenon which, in the light of known facts, is not in accord with an inactive source; for while this is not theoretically impossible, yet in the study of synthetical processes the formation of optically active compounds from inactive materials has not been noted.

While, previous to the knowledge of the presence of nitrogenous bases and of the optical properties of oil, many chemists supported the Mendeléeff hypothesis, some chemists and all the geologists, and especially Hoefer, accepted only the organic theory to explain its origin.

If the theory of the animal origin of oil was accepted it was still necessary to explain how oil containing very little or no nitrogenous materials could be formed from substances rich in this element, for an oil rich in nitrogenous materials was obtained by the distillation of fish. These observations and the known facts as to the great stability of the fats and waxes led to the suggestion by the author that the formation of oil from animal materials takes place in two stages, the first consisting in the destruction and removal of the nitrogenous compounds and nonfatty materials by fermentation processes, and the second in the conversion of the fatty residue into oil. In the formation from plants in a similar way the cellulose and related substances are first destroyed, leaving the fats and waxes, which later are changed into oil. This theory found confirmation in the work of Krämer, who found in some animal remains from sea mud, which had partly undergone decomposition, 20 per cent of fat when the normal amount in the live animal was 15.7 per cent; and in the work of Goedicke, who found that the fat content of a partly decomposed organism, whose normal amount in the living stage was 10 per cent, had risen to 18 per cent. It is of great interest and importance also that the author was able, in 1888, to obtain an almost quantitative yield of an oil having the general proper-

ties of petroleum by the distillation, under pressure, of fish, animal or plant fats, and even of synthetical glycerides and fatty acids.

This evidence produced a marked change of allegiance, on the part of chemists, from the inorganic to the organic theory. Soon, however, a new discussion arose as to whether the oil, acknowledged to be of organic origin, was formed from animal or vegetable materials. In considering the "vegetable hypothesis" it is necessary to make a distinction between the old view, according to which the oil was derived from the large plants of the uplands and from the carbon formed from these, and the more recent view, supported by Krämer, according to which the oil is formed from water and marsh plants, such as diatoms and algae. The weight of chemical and geological evidence is against the former; but as the possibility of the other theory is not denied, the statement is generally made that it is derived from both animal and vegetable sources. As a source of animal origin the macrofauna need not be considered as the most important, for Witt has called attention to the fact that the microfauna of the seas and shallow waters is also a very important source. The objection has been made to this theory that if the oil has an animal origin it should, on account of the immense amount of animal life in the seas, occur in much larger quantity; but just as in each age only a small proportion of the vegetable material was converted into coal, so only a small part of the fauna of each age may have been changed into bitumen and finally into oil. In describing the source of oil the term "fatty materials" must be used in the broadest way and understood as including liquid fats, waxes, rosin, balsam, cholesterin, tannic acid, and other substances of the same general nature. The nitrogenous matter is mostly destroyed and removed by fermentation processes and the carbohydrates must also be removed to a large extent, for the carbon formed from these is not found in the oil nor in the neighborhood of oil deposits. That the carbohydrates, however, do take some part in the formation of oil by first being changed to fats by the action of microorganisms has been established, and it makes no difference, from a chemical standpoint, whether this change is produced by microorganisms, macroorganisms, or foraminifera. In every case the nearest source is fat. Many of the objections to the author's theory are based on misconceptions. For instance, the objection has been made that the temperature (350°–400°) at which the experiments were generally carried out would in the natural process, on the

basis of an increase of 1° C. for every 33 meters, demand too great a depth at which the oil must have been formed. One author has calculated this depth to be 30,000 feet. Results obtained by a number of independent investigators have been uniformly lower than this value, the results obtained varying from 5. to 13.7 meters for each degree of temperature. The variations in the composition of oils is probably due to variations in temperature and pressure at the time of formation. In addition to the pressure due to the superimposed horizontal layers, a marked lateral pressure may be caused by faults, upheavals, etc., and produce a marked increase in temperature. Scheithauer found that where brown coal was subjected to a pressure of 1200–1500 atmospheres the temperature of the mass rose 80° to 100°.

Wepfer calculated that the pressure in the Alps due to faults was about 1720 times the compressive strength of granite, which is 1000 atmospheres per cm. The raising of mountain ranges or the depression of the floor of the sea would produce not only an enormous lateral pressure and an elevation of temperature, but in many cases a relative change in the position of the layers. The observation that oil is found along great mountain ranges is in harmony with these facts, and the occurrence of oil in deep layers in level country is not irreconcilable with them. In discussing the temperature necessary to produce the oil from plants and animals it should not be forgotten that time and temperature may compensate one another and that a change that is produced in a short time at a high temperature may be produced at a lower temperature in a long time.

The geologist and chemist regard the change of organic material into oil from different points of view. For example Potonié, a geologist, distinguished between the process leading to the formation of oil from water flora and fauna and the process by which land and swamp plants are converted into coal, while a chemist demands the exact mechanism of the changes and justly expects an answer. These questions can be answered in the following manner: The *first stage* of the changes into bitumen consists in a fermentation reaction during which the albumen and the cell substance of the plant disappear to a considerable extent. Only the fats, waxes, some fatty acids, and a small amount of other materials remain. In the *second stage* the saponification of the glycerides with the formation of free fatty acids is effected by the action of water or by fermentation, or both, and the esters of the waxes are also hydrolyzed. The residues in many oils are

probably due to incomplete decomposition. In a *third stage* the acids or esters decompose with formation of carbon dioxide, and the alcohols, oxalic acid, etc., with formation of water, leaving a residue consisting of complex hydrocarbons and some oxygen compounds. These substances have been regarded by some investigators as intermediate products. Next follows in a general way the formation of the liquid hydrocarbon mixtures of the oils by a violent reaction which causes the splitting up of the complex intermediate products with the formation of gaseous products. In these reactions a long continued low temperature could have produced the same results as a high temperature for a short time and it has been proved experimentally that the method of decomposition of complex fats and carbohydrates can be controlled by making changes in the temperature and pressure. The last change must have taken place at a high temperature and at a great depth, otherwise during the long time which has passed since these substances were formed the gases resulting from the decomposition of the complex compounds would have escaped. Thorpe and Young and others have shown that paraffin formed from saturated hydrocarbons gives, when decomposed under pressure, unsaturated hydrocarbons, so the presence of such compounds in oils can be readily explained. In the course of time and under the influence of a fluctuating temperature these unsaturated compounds form polymerization and addition products of high molecular weights and less liquid in nature, thus making another stage in the building up process of the oil. The author has found experimentally that such changes do take place, as there is a constant change in the specific gravity and other properties of the artificially prepared oils.

The hydrocarbon groups that would be represented according to this explanation of their formation would be as follows:

1. Members of the marsh gas series are formed directly by the decomposition of the "bitumen," this substance consisting of the product formed by the loss of carbon dioxide from the fatty residues and containing hydrocarbons of high molecular weights and some free fatty acids and esters.

2. Members of the ethylene series must be formed, for the complex saturated hydrocarbons would, by decomposition, give a simpler saturated compound and an unsaturated compound, thus: $C_{2n}H_{4n+2} = C_nH_{2n+2} + C_nH_{2n}$. On account of the unsaturated nature of these compounds and of their strong power of forming polymeric and addition products, or else due to the changes produced by distillation, these hydrocarbons would, in course of time, disappear.

3. It is highly probable that the large amount of naphthene present in some varieties of oil has been formed by the decomposition by heat and under pressure of certain aromatic acids or esters or of a number of other compounds. The view held by the author and by Krämer that the naphthene might be formed also by the action of heat and pressure on the primary olefine has been experimentally confirmed by Aschar who obtained a hexanaphthene and higher homologues by the action of aluminium chloride on amylene. The author then confirmed this result by subjecting an olefine to a high temperature in a sealed tube for some days.

4. The lubricating oil is a mixture of saturated and unsaturated hydrocarbons of a number of series. This could have been formed in three ways and perhaps all of these may have played a part in its formation. It may have been formed by direct decomposition of the fatty residue, for Engler and Singer found experimentally that an oil of this kind was formed in a case where fish blubber was distilled under pressure. Of greater importance, however, is the method which depends upon the self polymerization and addition of the unsaturated compounds formed by the decomposition of the organic residues, for these substances, in their unsaturated condition, could not remain separate if in close contact. The author, unlike LeBel and Heusler, does not consider that catalysis is necessary to produce this change, for he has found that the unsaturated compounds, by the action of heat and pressure, pass over into high boiling, viscous oils when only a small amount of aluminium chloride is present. A synthesis by Krämer and Spilher supports the view held by the author.

5. Benzene and its homologues, which are found in different oils in widely differing amounts, could have been formed by the decomposition of the fatty material at a moderate temperature. The author and Lehmann, by the distillation of blubber, obtained benzene, toluene, *m*-xylene, pseudocumene, and mesitylene. In the natural process of oil formation this action must take place at 300°–400°. Albumens and phenylacetic ester both form benzene hydrocarbons. The author does not consider the view, held by Bertels, Radziszewsky, and others, that petroleum was formed exclusively by fermentation processes, to be tenable. While bacteria and enzymes play a very important part in many transformations it is not a safe conclusion, so far as oil is concerned, that this has been the only force at work.

Evidence presented by G. Meyer, who found petroleum in certain deposits formed by bacterial action, and C. B. Morrey,

who found fossil bacteria in oil-bearing rocks, are considered by the author as of little weight, as they are either not yet conclusively proved or can be readily explained on his theory. No direct evidence has been found for this view, while against it is the experimental observation that when cinnamic acid is treated with *Penicillium glaucum* or *Aspergillus niger* the product formed is almost entirely marsh gas and never oil-like hydrocarbons, with the exception of traces of styrene. The fact that high temperatures are not favorable to bacterial action and that the soil acts as a bacterial filter would be against the possibility of the formation of oil by such action in the lower deposits and at high temperatures. There is in fact an overwhelming mass of evidence in favor of the view that it is only in the first part of the process that fermentation plays any part.

The Origin of the Optically Active Constituents.—The activity must be due to the presence of an active residue of the original strongly active source or of the residue of the activity produced in the formation of the substance, as optically active opposites generally form an inactive substance. Walden based his view of the vegetable origin of petroleum on the ground that the oil, like many active vegetable materials and especially a fossil vegetable material, showed nearly always righthanded activity. The author says that the activity of the original substance and the derivatives is not always the same, that there are many righthanded animal derivatives, and that the plantlike fossil upon which the view was largely based was probably not derived from fat, but from rosin.

Neuberg suggested albumen as the source of the active constituents of petroleum; but the substances formed by its decomposition are chiefly products of low molecular weights, while the active constituents of oil are high molecular compounds. Neuberg pointed out, however, that from an optically active fatty acid and a high molecular inactive fatty material an active oil could be obtained. The author at first considered the activity of the oil to be due chiefly to admixture with a single substance, but later found that in a great number of cases, where the boiling temperature, under diminished pressure, of the active fraction was being studied, the activity increased to a maximum and then decreased as the temperature was raised. In most cases this maximum point occurs with the portion boiling between 200°–300°. In some cases two maxima were observed with inactive portions lying between. In a sample of oil from Java the lower boiling portions were laevorotatory, then followed an inactive portion,

which was followed in turn by a dextrorotatory oil. These reactions can be best explained by the assumption that the activity is due to *cholesterin.* A number of investigators have studied this problem and while some have pointed out the similarity of the product obtained from cholesterin with the oil, others have found that the products formed by the distillation of cholesterin are dependent upon the way in which the distillation is conducted. For example, when this substance was heated for one hour to 350° the product was strongly dextrorotatory, while when heated to 300° no marked change from the laevorotatory condition could be noticed. Between 300°–350° in the course of one hour the marked change from the laevo to the dextro condition occurred. Phytosterin behaved in a similar way to the cholesterin.

The results obtained by Albrecht in an investigation of the optically active portion of Galician oil showed that only a very small amount of cholesterin need be present to explain the activity of the oil. In the formation of oil the amount of chlolesterin destroyed was small as compared with the amounts of fatty and waxlike residues lost, thus causing a natural concentration of the active constituents. Neuberg's objection to this explanation that the organic materials in the earth are not rich enough in cholesterin to account for the amount necessary has been rendered untenable by the discovery by Marcusson of rich sources of this substance in nature. As further proof that cholesterin is the cause of the activity the author cites the great similarity in the behavior of an artificial oil made up of inactive components and cholesterin to that of the natural oils, and also the similarity of Java oil to the cholesterin distillate, the dextro and laevorotatory substances being obtained not only in the same order but at the same temperature in the two materials. Still stronger confirmation was furnished by the experiments of the author and Lederer. As before mentioned, with cholesterin the laevo distillate on heating becomes a dextrorotatory substance. The laevorotatory portion of Java oil is derived from the cholesterin; but does not become dextrorotatory when heated. If it is sealed in a tube and heated it does change to the dextro variety. Unless this process is very carefully carried out the dextro variety, by racemizing or by some other method, is destroyed. Moreover, that the optically inactive portion is really made up of equally strong dextro and laevo components is shown by the fact that by the same process as described above this inactive portion becomes dextrorotatory, owing to the change of the

laevo portion to the dextro variety. These observations suggest the possibility of the inactive oils being racemic varieties of the two active varieties and that all optically active oils in the course of time, or more quickly when heated, pass over by one of several possible methods into an inactive form, thus making the active oils transition products not completely changed. The author closes by acknowledging that perhaps some oil may have been formed from inorganic source; but he believes that the main supply is of organic origin, vegetable or animal, or both.   J. E. G.

PREPARATION OF SALTPETER BY THE PROCESS OF THE BAD-ISCHE ANILIN- UND SODA-FABRIK.[1]

To meet the ever-increasing demand for nitrogenous fertilizers, three sources of nitrogen are available: (1) Ammonia formed in the preparation of coke and gas by the distillation of coal; (2) the Chile saltpeter beds; and (3) the inexhaustible supply of nitrogen in the air. As the ammonia obtained from coal is merely a by-product, and the saltpeter beds are rapidly nearing exhaustion, the problem of the fixation of atmospheric nitrogen is becoming more and more important, and several methods by which this can be accomplished have been successfully worked out. Of these, two are now familiar to every one: first, the cyanamide process, based on the absorption of nitrogen by heated calcium carbide, with formation of calcium cyanamide; and secondly, the Birkeland-Eyde process for the manufacture of nitrates. It has been known since the time of Priestley and Cavendish that when electric sparks are passed through moist air the nitrogen combines with the oxygen, and nitric acid is formed. According to our present views, this reaction is a purely thermal one and is in no way due to any specific property of electrical energy. As in all endothermic reactions, *i. e.*, such as are accompanied by absorption of heat, the higher the temperature the greater the amount of reaction product, in this case nitric oxide, which is formed. Thus, for example, at 3000°, 4.5 per cent, by volume, of nitric oxide can be obtained from air, but at 1800° only 0.7 per cent is formed. The reaction is reversible, and not only does the velocity of formation of the nitric oxide increase with the temperature, but the reverse dissociation into nitrogen and oxygen does also. In order, therefore, to obtain the maximum possible amount of nitric oxide, the mixture of oxygen and nitrogen must first be heated to a high temperature

and then suddenly cooled to avoid loss through the dissociation of the nitric oxide. In the Birkeland-Eyde process this object is attained by forcing the air at right angles through an electric arc so deflected by powerful magnets as to offer as large a surface as possible. The process of the Badische Anilin- und Soda-Fabrik is based on the same principle, but instead of being forced through the flame, the air is carried along a quietly burning arc of great length. The apparatus used consists essentially of a tube whose end is connected to one pole of the machine furnishing the current, while at the other end of the tube, but isolated from it, is placed an electrode connected to the other pole of the machine. The arc is now lighted, usually by making the distance between the electrode and the wall of the tube sufficiently small, and the air is forced in at a tangent so that it passes through the tube with a spiral or whirlwind motion. It carries along one end of the arc before it until it reaches the end of the tube, when the arc continues to burn quietly in the center of the tube while the air rapidly whirls around it. In this way arcs 5 meters long are produced and burn quietly for weeks at a time without relighting. The company has now three furnaces, with a total of about 2000 horse-power, in operation in Christianssand in southern Norway. The furnaces are very durable, the only part which suffers rapid deterioration being the lower electrode which either consists simply of iron rods or may be constructed of conductors of the second class, such as zircon oxide. In this process there is less waste of electrical energy and the nitrogen oxides are obtained in greater concentration than in all other known processes. The Badische Anilin- und Soda-Fabrik has combined with the owners of the Birkeland-Eyde process for the manufacture of nitrates, and plants having an aggregate of 120,000 horse power are in course of construction in Norway.   c. a. r.

REVIEWS.

THE CHEMISTRY OF THE DIAZO-COMPOUNDS. By JOHN CANNELL CAIN, D. Sc. (Manchester and Tübingen); Editor of the Publications of the Chemical Society; Joint Author of "The Synthetic Dyestuffs and the Intermediate Products from which They are derived." London: Edwin Arnold. 1908. pp. x + 172.

Chemists will find this small book an excellent guide to the study of the diazo-compounds. The author says: "I have endeavored to describe our present knowledge of the Diazo-compounds and to give an account of the enormous progress made in this important branch of Organic Chemistry since Griess's epoch-making discovery just fifty years ago."

The literature of the subject is very confusing but the author has evidently studied the original articles carefully and dealt with the material in a fair-minded way. Referring to the principal causes of the confusion he says: "I have striven to give an exact account of the long controversy between Hantzsch and Bamberger on the constitution of the diazo-compounds. The most important contributions to the literature have hitherto been made by Hantzsch (*Die Diazover-bindungen*, Ahrens' Sammlung, 1902) and his former pupil, Eibner (*Zur Geschichte der aromatischen Diazoverbindungen*, Oldenbourg, 1903), so that the opposite view has, perhaps, not been set forth quite so fully, although the admirable Report to the British Association by Morgan (*Our Present Knowledge of Aromatic Diazo-compounds*, 1902) leaves nothing to be desired."

Full references to the literature are given and apparently this part of the work has been done conscientiously. The book is warmly recommended to teachers and students.

I. R.

SYNTHETISCH-ORGANISCHE CHEMIE DER NEUZEIT. Von DR. JULIUS SCHMIDT, A. O. Professor an der Königl. Technischen Hochschule Stuttgart. Braunschweig: Vieweg und Sohn. 1908. Seiten x + 185 Preis: geheftet, M. 5.50; geb. in Leinwand, M. 6.20.

The ground covered by this excellent treatise can best be indicated by giving the titles of the different chapters.

Chapter I. Importance of the organomagnesium halides for synthetic purposes.

Chapter II. Some synthetic results in the sugar group. Asymmetric synthesis.

Chapter III. Synthetic reactions which give aldehydes and ketones.

Chapter IV. Dimethyl sulphate as a methylating agent.

Chapter V. Syntheses by means of azides.

Chapter VI. E. Fischer's methods for the synthesis of polypeptides.

Chapter VII. Syntheses by the splitting off and transformation of cyclic bases.

Chapter VIII. Syntheses in the field of the alkaloids, of artificial medicinal agents, and in the purine group.

Chapter IX. Syntheses of dyes and of polynuclear aromatic compounds.

Chapter X. Syntheses of perfumes, of hydroaromatic and related compounds.

Chapter XI. Electrolytic syntheses of various organic compounds.

No synthetic reaction has ever found such rapid and extensive application as that which we owe to Grignard. It is, however, surprising to learn that in the period of eight years more than 450 articles have appeared that have to deal with the application of organic magnesium compounds of the type R. Mg. Hlg to synthetic purposes.

Regarding the influence of the introduction of synthetic indigo in the production of natural indigo we learn that in 1902 the production in Bengal had fallen off 48 per cent. In 1902 the quantity of natural indigo, estimated as 100 per cent indigo blue, amounted to 3 millions of kilograms while the quantity of the artificial indigo was 5 millions of kilograms. The price of pure indigo blue which, before the introduction of the artificial product, was from 16 to 20 marks a kilogram fell towards the end of 1905 to 7 to 8 marks.

The artificial preparation of camphor has long been the subject of investigation. It is stated that a Berlin firm has recently put upon the market considerable quantities of this product. All methods for its preparation that are of practical interest start with pinene. The importance of the problem involved is shown by the following statement of A. Hempel: "The world's consumption of camphor is calculated at 3 to 4 millions of kilograms per year, of which 1 million falls to Germany. * * * * At present the price of camphor is 1000 marks for 100 kilograms. In spite of this known actual valuation the Japanese monopoly furnishes the principal consumers, the celluloid manufacturers and refiners, crude camphor containing 90 per cent at 450 marks.

"It may confidently be assumed that Japan will meet competition by low price as soon as the artificial product is put upon the market. The prices may then fall to the level reached in 1898, perhaps below 200 marks."

The book is interesting and valuable.   I. R.

THE CHEMICAL BASIS OF PHARMACOLOGY. An introduction to Pharmacodynamics based on the Study of the Carbon Compounds. By FRANCIS FRANCIS and J. M. FORTESCUE-BRICKDALE. London: Edward Arnold. 1908. pp. 372. Price, $4.

The correlation of pharmacological action with the structure of chemical compounds has long proved an attractive field of investigation for both pharmacologist and chemist, but it must be confessed that the generalizations which it has been possible to formulate as a result of studies of this nature have seldom proved capable of wide application. This is due in part to insufficient experimental results but also to lack of coöperation between the chemist and pharmacologist. The

present volume is of special interest owing to the fact that one of the authors (Professor Francis) is well known for his researches in pure organic chemistry, while the other author is primarily a clinician. It must be admitted, however, that despite certain admirable sections, the book as a whole is disappointing.

The arrangement of the material commencing with the chapters dealing with general chemical and physiological principles, followed by sections on the fatty and aromatic hydroxy compounds and their derivatives, and lastly those dealing with the more complicated nitrogen-containing substances, leaves little to be desired. An interesting account is given of the various urethane and urea derivatives which possess marked hypnotic properties and some of which are actually employed in practical therapeutics. Of these the product introduced by Emil Fischer and von Mering, known as "Veronal" (diethylbarbituric acid), appears to be the most important. It is stated to surpass in intensity of action all the hypnotics hitherto employed and the cost of an effective dose is less than that of any other hypnotic except chloral hydrate.

The later chapters deal with the alkaloids, glucosides, and synthetic substitutes for cocaine, atropine, etc., and the book closes with a section in which the dependence of taste and odor upon chemical structure is discussed.

It is surprising to find adrenalin placed under the heading of "Substitutes for Hydrastis," as is also the statement that the extract prepared from suprarenal glands, which contain the adrenalin, is "the most important body *recently* introduced into medicine." As a matter of fact the extract has been in common use for about ten years and the crystalline active principle was obtained by Takamine and Aldrich in this country in 1901.

The work might have been greatly improved by adequate proof-reading and by more careful reference to the original sources of information. It is perhaps due to the authors to give specific examples of these inaccuracies. Taking a few consecutive pages at random one finds for example on p. 68 that *β-oxypropylaldehyde* is converted by oxidation into *β-oxybutyric* acid and on the same page the formulae for butyric aldehyde and butyric acid are incorrectly given. On the following page the statement concerning the fate of formic acid in the body is misleading, while the information on page 73 as to the combustion of oxalic acid in the tissues contains no reference to recent work. On page 72 the substance C_2H_5.

HSO$_4$ is incorrectly named, while on page 75 the statement implying the absence of sulphocyanide excretion following acetonitrile administration is incorrect, as is also the statement, on the same page, that only two benzene derivatives are present in the protein molecule, no account being taken of tryptophane (indoleaminopropionic acid). The assertion that α-phenylpropionic acid gives rise to homogentisic acid in cases of alcaptonuria is also without basis in fact. An account is given on page 77 of Knoop's investigations of the mechanism of animal oxidation which omits the more important observations, and the statement that phenyl fatty acids, other than phenylpropionic acid, with more than two carbon atoms in the side chain do not yield benzoic acid is incorrect, since Knoop's crucial experiment upon which the theory of β oxidation is largely based consisted in the observation of the excretion of benzoic acid (hippuric acid) after administration of phenylvaleric acid.

Enough has been written to show that the book requires a large amount of careful revision before it can hope to attain any great measure of success.   H. D. DAKIN.

ELEMENTS OF WATER BACTERIOLOGY, WITH SPECIAL REFERENCE TO SANITARY WATER ANALYSIS. By SAMUEL CATE PRESCOTT and CHARLES EDWARD AMORY WINSLOW. Second edition, rewritten. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1908. pp. XII + 258. Price, $1.50.

The first edition of Prescott and Winslow's little book on Water Bacteriology has proved an exceedingly useful guide to workers in this field, representing, as it did, the concensus of opinion of the best American bacteriologists. We are therefore especially glad to see a second edition considerably larger and more comprehensive than the first. In addition to a new chapter on the Bacteriology of Sewage and Sewage Effluents, several chapters have been rewritten and brought up to date, namely, those dealing with methods of isolation of typhoid bacillus, the presumptive tests for *B. coli* and the significance of intestinal bacteria, other than *B. coli*, in suspected water.

The present edition may be most cordially recommended to students.   W. W. FORD.

THERMOELEMENTE UND THERMOSÄULEN. Ihre Herstellung und Anwendung. Von PROFESSOR DR. FRANZ PETERS, Dozent an der Königlichen Bergakademie zu Berlin. Mit 192 in den Text gedruckten Abbildungen. Halle a. S: Verlag von Wilhelm Knapp. 1908. pp. 180.

This number of the " Monographien über angewandte Elektrochemie " brings together in a convenient and scientific

form what is known in reference to thermoelements. It is probably the most satisfactory treatise on this subject that has ever been written and since it includes what was published even in the first half of the year 1907 it is fully up-to-date.

The section dealing with the various chemical elements used in making thermoelements is the most interesting reading. The following metals are mentioned as electrodes: aluminium, antimony alloys, metals of the cerium and chromium groups, iron, copper, nickel, and nickel alloys, platinum, silicon, tellurium, bismuth, zinc. Copper sulphide, lead sulphide, carbon, etc., are also used.

This monograph seems to be of the same high standard as the other volumes of this series. H. C. J.

DIE CHEMISCHE AFFINITÄT UND IHRE MESSUNG. Von DR. OTTO SACKUR, Privatdozent an der Universität Breslau. Mit fünf Abbildungen im Text. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1908. pp. 129.

This interesting and important monograph is one of "Die Wissenschaft" series. The problems dealt with are those which lie right at the basis of chemical science. As the author states in his preface, chemists have recognized the importance of thermodynamics for chemistry ever since Van't Hoff pointed out that the measure of the chemical forces manifested between reacting substances is the maximum work which the transformation in question can do. Sackur expresses his indebtedness for the thermodynamic developments to Nernst, Blanck, and Haber. "I hope," says he, "that I have succeeded in presenting clearly the great advance which chemistry owes to thermodynamic methods of dealing with chemical problems, and thus have furthered its general recognition;" and a careful study of this monograph will show that this hope has been realized.

The subject is treated in six chapters. The first is a historical development of the conception of chemical affinity. The second deals with the principle of maximum work and the second law of thermodynamics. The third chapter has to do with the calculation of affinity from the amount of the transformation; the fourth with the electrical method of measuring affinity; the fifth with affinity and temperature; and the sixth and last chapter gives some results of the measurement of affinity—results from reactions between compounds, and from reactions between the elements.

With the exception of the first and last chapters the monograph is literally filled with differential equations, and this suggests a thought which has doubtless occurred to every

teacher of advanced chemistry. That is, the desirability, indeed, the absolute necessity of a good elementary knowledge of the so-called higher mathematics, in dealing with the fundamental problems of chemical sciences.

It is still true that one can learn much about the empirical facts of chemistry without a knowledge even of the calculus, just as one can learn something about the empirical facts of physics without any extended knowledge of mathematics. But as no one can even approach the fundamental principles underlying the science of physics without a good knowledge at least of differential equations, so, also, is it impossible to master the fundamental principles underlying chemistry as a science without an elementary knowledge of thermodynamics.

It is difficult to overestimate the importance of impressing these facts upon students of chemistry who are just beginning their careers.   H. C. J.

AMERICAN

CHEMICAL JOURNAL

THE ACTION OF CHLORINE UPON UREA, WHEREBY A DICHLORUREA IS PRODUCED.[1]

By Frederick Daniel Chattaway, F.R.S.

Although a few of the more familiar substances containing halogen attached to nitrogen, as, for example, nitrogen chloride, have been known for a long period, it is only within the last 10 years that such compounds have been systematically studied. They form, however, a group of extraordinary interest and play an all-important part in many complex reactions; to illustrate this it is only necessary to refer to the substitution of halogen in anilides and to the well-known method for obtaining amines from amides. I have shown in a series of investigations that hydrogen attached to nitrogen in compounds of the most varied characters may be replaced with ease by chlorine or bromine if suitable conditions are observed, and it may be said, speaking generally, that this can always be done, although the nitrogen halogen derivatives produced may react or undergo isomeric change so readily that they can only with difficulty be isolated.

All compounds in which halogen is directly attached to tri-valent nitrogen can take part in certain well-defined reactions characteristic of the linkage. One of the most striking of these group reactions is that with hydriodic acid, whereby at the ordinary temperature the halogen is replaced by hydrogen, and iodine is liberated quantitatively. This reaction, which may be expressed by the general equation

$$: NX + 2HI = :NH - HX + I_2,$$
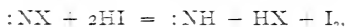
affords an easy method of analyzing these compounds.

Such a nitrogen halogen derivative is formed as an inter-mediate product in a reaction with urea, the course of which has never hitherto been explained although it has received an unusual amount of attention as it furnishes a ready method of estimating the quantity of the urea present in a liquid.

When urea is added to a solution of an alkaline hypochlor-ite or hypobromite it is at once decomposed, nitrogen and car-bon dioxide being set free; if an excess of alkali is used the carbon dioxide is fixed, and the nitrogen, which alone escapes, should thus afford a measure of the amount of urea. The re-action is generally represented by the equation

$$CO(NH_2)_2 + 3NaOBr = CO_2 - N_2 + 3NaBr + 2H_2O,$$

which throws no light upon its nature; indeed it obscures it, as it makes it appear to be a case of oxidation. It does not even express quantitatively what takes place, for all chem-ists who have investigated the decomposition have noted that the amount of nitrogen liberated is invariably less than that contained in the urea used. When the operations are carried out under specified conditions this loss of nitrogen, which may amount to as much as half of the total, is very constant and so can be allowed for by adding a definite frac-tion of the whole to the gas actually measured. The method can thus be made to give results sufficiently accurate for clin-ical purposes and since it is easy to carry out it has received very general application. It is not known what becomes of the nitrogen which does not appear as gas, for all the sug-

gestions that have been made hitherto wholly fail to account for more than a small fraction of the quantity that disappears.

If the urea, instead of being added to an alkaline solution of a hypochlorite, is added to one acidified by acetic acid, that is, to a solution of hypochlorous acid, no gas is evolved, nor is any gas liberated if chlorine itself is passed into a solution of urea in acetic acid. Action takes place, however, in each case and a nitrogen chloride is produced; for although the hypochlorous acid or chlorine disappears, the resulting solution liberates iodine in large quantity from hydriodic acid.

The isolation from such a solution of the substance produced is not practicable, since the method of extraction by chloroform which often serves for the separation of substituted nitrogen chlorides cannot be used, as the chlorurea formed is easily soluble in water but almost insoluble in chloroform. It is, however, less soluble in water than urea itself and crystallizes out in a pure condition when chlorine in excess is passed rapidly through a cooled and sufficiently strong aqueous solution of urea. The action which takes place is represented by the equation

$$CO\diagup^{NH_2}_{NH_2} + 2Cl_2 = CO\diagup^{NHCl}_{NHCl} + 2HCl,$$
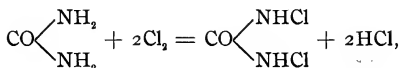
two only of the four hydrogen atoms of the urea being replaced by chlorine.

This dichlor derivative appears to be the only stable nitrogen chloride which urea is capable of forming. The crystals which separate from the solution of urea have this composition from the first and chlorine seems to have no further substituting action upon them.

Considering its mode of formation, as well as the structure of urea itself, dichlorurea has most probably the constitution represented by the formula $O : C\diagup^{N<^{Cl}_{H}}_{N<^{H}_{Cl}}$, which explains its formation and such of its reactions as have so far been studied.

If this constitution be granted it seems probable that the reaction between urea and chlorine takes place in two stages and that the amino groups are substituted successively, but the monochlor derivative does not crystallize out, possibly because its solubility is not far removed from that of urea itself. Either of two causes may prevent the formation of a tri- or tetrachlor derivative; the hydrochloric acid which is formed in the reaction may prevent the addition of chlorine to the nitrogen which must precede further substitution, or the more highly substituted urea may be hydrolyzed so easily that it breaks up as soon as it is formed. Dichlorurea is so much more easily hydrolyzed than urea itself that the latter is the more probable cause.

Although two molecules of hydrogen chloride are formed when chlorine acts on urea, very little heat is developed. Dichlorurea must, therefore, be an endothermic compound and might be expected to be highly explosive. When heated, however, it does not itself explode but decomposes with liberation of nitrogen chloride which, if heated to a few degrees above the temperature at which it is set free, may detonate with great violence.

Dichlorurea gives all the characteristic reactions of a typical nitrogen chloride; for instance, it liberates iodine from hydriodic acid and chlorine from hydrochloric acid, and reacts with alcohol, forming ethyl hypochlorite, urea being in each case re-formed.

It is distinguished from most other substituted nitrogen chlorides by the readiness with which it is hydrolyzed in presence of water, with formation of nitrogen chloride, carbon dioxide, a little nitrogen, and ammonium chloride. If the compound is dissolved in water or kept in a moist atmosphere, this hydrolysis takes place slowly at the ordinary temperature and becomes very rapid at about 30° C.

It is probable that in this reaction a monosubstituted ammonia is first produced, thus:

$$CO\begin{cases} NHCl \\ NHCl \end{cases} + 2H_2O = CO\begin{cases} OH \\ OH \end{cases} + 2NH_4Cl \, ;$$
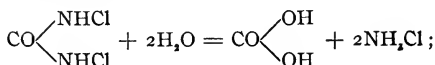
but if it is, it apparently can exist only momentarily, as nitrogen chloride is at once liberated. The formation of the end products of the reaction can be explained by assuming that this monochlorammonia at once breaks up into ammonia and nitrogen chloride,

$$3NH_2Cl = 2NH_3 + NCl_3,$$
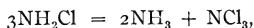
which then react to some extent, forming nitrogen and hydrogen chloride, the latter at once combining with the free ammonia and allowing the remaining nitrogen chloride to escape, as this does not react with ammonium chloride. Both acids and alkalis accelerate the rate of hydrolysis and also alter the nature of the end products by hindering or furthering the secondary reaction between the ammonia and the nitrogen chloride.

In presence of dilute acids the ammonia is at once fixed and the reaction between it and the nitrogen chloride, with its accompanying liberation of nitrogen, is prevented, all the chlorine contained in the dichlorurea being therefore liberated as nitrogen chloride. In presence of alkalies, on the other hand, the reaction between the ammonia and the nitrogen chloride goes on to completion, since the hydrochloric acid formed in it is at once fixed; no nitrogen chloride, therefore, is set free, since twice as much ammonia is formed as is required to decompose it.

The reaction between dichlorurea and a solution of caustic potash is instantaneous: nitrogen is liberated with violent effervescence, the excess of ammonia and the alkaline carbonate formed remaining dissolved in the liquid. The action, which is quantitative, is expressed by the equation

$$3CO\begin{subarray}{l} \diagup NHCl \\ \diagdown NHCl \end{subarray} + 12KOH = 3K_2CO_3 + 2NH_3 + 6KCl + 2N_2 + 6H_2O.$$
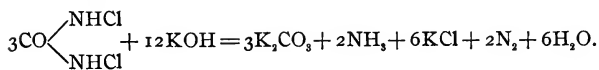
The behavior of dichlorurea with alkalis affords an explanation of the course of the reaction which occurs when urea is decomposed by an excess of either alkaline hypochlorite or hypobromite. The urea is, without doubt, converted into

dichlor- or dibromurea,[1] which is at once hydrolyzed in the manner above described. In presence of the excess of hypochlorite or hypobromite, the monosubstituted ammonia formed in the hydrolysis may be further substituted to a greater or less extent, nitrogen being evolved quantitatively only when this takes place under such conditions that the amount of hydrogen attached to nitrogen in the reacting system is always sufficient to react completely with the chlorine attached to nitrogen.

Preparation of Dichlorurea.—The preparation of dichlorurea should be carried out at a low temperature and as rapidly as possible, since, in presence of the hydrochloric acid formed at the same time, hydrolysis so readily occurs and so much nitrogen chloride is produced that if it is carried out at the ordinary temperature, or its duration is unnecessarily prolonged, a poor yield is obtained. It is best, therefore, to work with small quantities, to cool thoroughly, and to pass the chlorine as rapidly as possible. The following procedure gives a good result: Dissolve 20 grams of urea in 40 cc. of water and cool to about −10° C. in a mixture of alcohol and crushed ice.[2] Pass in as rapidly as practicable a stream of chlorine made by dropping strong hydrochloric acid upon bleaching powder. So little heat is evolved in the reaction that with proper cooling the temperature never rises above zero, however rapid the stream of chlorine. Nitrogen chloride is produced from the first and can be recognized by its characteristic smell, but it remains in solution, the liquid, owing to its presence, becoming bright yellow in color. After passing the chlorine for a considerable time, white crystals make their appearance, at first usually on the surface of the liquid; these increase in amount till the whole becomes a pulp of thin,

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[1] It is possible that in absence of free acid, and in presence of excess of hypochlorite or hypobromite, a tri- or tetrahalogen substitution product may be produced, the formation and decomposition of which can be formulated easily, but this does not affect the essential character of the reaction, which is one of halogen substitution followed by hydrolysis of the substituted urea and interaction between the resulting compounds.

[2] It is not absolutely necessary to use a freezing mixture. The temperature, owing to the solution of the urea, falls at once to below zero, and if the flask in which the operation is carried out is cooled by tap water, a moderate amount of the compound can be obtained, but the yield is much better at a lower temperature.

colorless plates. When these no longer appear to increase in amount, filter off, separating the acid mother liquor as completely as possible; wash once or twice with a little water, and when as much of the latter as possible has been removed wash the crystals several times with dry chloroform. Dichlorurea is not appreciably soluble in cold chloroform and a good deal of adhering moisture is thus got rid of. Press finally between filter paper, spread out in a thin layer on a clock glass, and free from the last traces of water by exposing for about half an hour over phosphoric oxide in a vacuum.

A further crop of crystals can be obtained by again passing chlorine through the cooled mother liquor and this can be repeated as long as any crystals separate. Nothing besides dichlorurea and the products of its hydrolysis are formed in the reaction; if the acid mother liquor is evaporated down, carbon dioxide is given off and nitrogen chloride escapes in quantity; later, as the liquid becomes concentrated, hydrogen chloride is expelled, and finally ammonium chloride is left.

Although the final result of the action which takes place is the substitution of two atoms of hydrogen by two atoms of chlorine, as in other similar cases this is without doubt effected by the addition of four atoms of chlorine to the nitrogen, followed by the elimination of two molecules of hydrogen chloride.

So much of the dichlorurea is hydrolyzed during the process that the yield is not very large: in a well conducted experiment it reaches about 25 per cent of the calculated, the weight of pure dry product obtained amounting as a rule to rather more than half the weight of the urea used. The loss, although largely due to the hydrolysis of the compound, is much increased by the circumstance that dichlorurea is very soluble in water and consequently a considerable amount does not crystallize out from the mother liquor.

Dichlorurea acts with an aqueous solution of hydriodic acid in the way characteristic of nitrogen chlorides; urea is re-formed and iodine quantitatively liberated. It was analyzed by taking advantage of this reaction: a known weight was added to an excess of a solution of potassium iodide made acid

by acetic acid and the iodine liberated estimated by a standard solution of sodium thiosulphate.

0.5112 gram liberated iodine = 158.6 cc. N/10 I.

	Calculated for $CON_2H_2Cl_2$.	Found.
Cl as : NCl	54.96	54.99

Dichlorurea cannot be kept for any length of time without change. When damp it hydrolyzes exactly as when dissolved in water. To obtain it pure, therefore, it must be dried very rapidly over phosphoric oxide in a vacuum. When freed from adhering water only as far as is possible with a pump, it is slowly hydrolyzed by the retained moisture even though placed in a desiccator over strong sulphuric acid, and this often occurs to such an extent that the mass becomes quite yellow from the nitrogen chloride mechanically retained by the crystals. To show the amount of hydrolysis which takes place under these conditions a quantity of the pure substance thus freed from all but adhering water was kept over strong sulphuric acid, and analyzed from time to time, the nitrogen chloride formed being allowed occasionally to escape. In two days the percentage of chlorine as : NCl had fallen to 43.79, and in seven days to 13.33.

Even when dried and kept over phosphoric oxide it slowly decomposes, nitrogen chloride being evolved. A quantity of the pure dry compound thus preserved in a vacuum over phosphoric oxide was analyzed at intervals; after 12 hours the percentage of chlorine as : NCl had fallen to 54.67, after two days to 52.97, and after nine days to 47.87 per cent.

When an aqueous solution is kept at the ordinary temperature the dichlorurea is slowly hydrolyzed; carbon dioxide, a little nitrogen, and nitrogen chloride escape, and ammonium chloride remains in solution. Complete hydrolysis by water requires many days unless the aqueous solution is warmed, when it is much more rapid; at about 20° bubbles of gas are freely evolved and rapid effervescence sets in at about 40°, the nitrogen chloride escaping without explosion.

Dichlorurea prepared as described above is a soft, white, crystalline power with a pearly lustre. Under the microscope

it is seen to consist of thin transparent plates somewhat irregular in shape. It can be recrystallized from water, in which it is easily soluble and from which it separates in similar but larger plates, by cooling an aqueous solution saturated at about 15° C., though there is some loss owing to hydrolysis. Its aqueous solution is at first colorless but becomes yellow as hydrolysis proceeds, owing to the liberation of yellow nitrogen chloride which remains dissolved in the water. It is easily soluble in alcohol and ether, very slightly soluble in chloroform, and soluble in petroleum ether. When its alcoholic solution is heated it reacts in the way characteristic of nitrogen chlorides, urea is re-formed, and ethyl hypochlorite is produced, the latter very easily breaking down into aldehyde and hydrogen chloride.

Its behavior with acids is complicated by the circumstance that it is so readily hydrolyzed; for example, when it is added to strong hydrochloric acid, though chlorine is rapidly given off, the amount of urea re-formed is not very large. When placed in cold strong sulphuric acid it is hydrolyzed and nitrogen chloride is liberated. The latter decomposes into its elements if the liquid be heated, its characteristic smell disappearing and being replaced by that of chlorine.

Dichlorurea is a compound of a marked acid character; it has an acid taste recalling that of hypochlorous acid, and its aqueous solution strongly reddens litmus paper, which becomes bleached only after the lapse of some minutes. It acts very corrosively upon the skin, staining it yellow and destroying the tissues.

When heated, dichlorurea melts with decomposition at about 83°, nitrogen chloride being liberated. Although the substance itself appears not to explode, if the temperature of the bath in which the melting point is being taken is allowed to rise at all rapidly a few degrees above this point, the nitrogen chloride set free in the tube may explode with considerable violence.

If thrown in quantities of not more than about half a gram at a time into a porcelain dish heated to 100° on a water bath, it can be decomposed without danger. The white

compound fuses and gives off nitrogen chloride as a yellow
vapor which escapes quietly unless too large a quantity of ma-
terial is decomposed at once, when some of the vapor is mechan-
ically retained as bubbles in the semifused residue and thus
becomes heated to the temperature at which it explodes.
Hydrogen chloride is not set free when dichlorurea is thus de-
composed by heat.

When an aqueous solution of the compound is added to a
solution of caustic soda vigorous effervescence, due to escape
of nitrogen, occurs. The liquid remaining contains ammonia
and potassium carbonate, the volume of carbon dioxide lib-
erated when this is treated with an acid being to the volume
of nitrogen previously liberated as 3:2. One third of the nitro-
gen contained in the dichlorurea used is found as am-
monia.

The investigation of dichlorurea, which is an extremely
reactive body and promises to be of considerable use in or-
ganic synthesis, is being continued.

The thanks of the author are due to Dr. Baker for allow-
ing him to use the Christ Church Laboratory, where this
work has been carried out.

THE REGULATION OF TEMPERATURE IN THE MEAS-
UREMENT OF OSMOTIC PRESSURE.[1]

By H. N. Morse and W. W. Holland.

The more recent improvements in the manometers and
cells which are used in the measurement of osmotic pressure
have already been described.[2] The subject of the present
paper is the methods which have been adopted for the pur-
pose of securing constant temperatures in the various baths
employed in the work.

The regulation of temperature in the measurement of os-
motic pressure presents certain unusual difficulties, the grav-

ity of which appears not to have been fully realized by most of those who have attempted to measure the force. The principal source of these peculiar difficulties lies in the fact that the osmotic cell, filled, as it is, with a considerable volume of a liquid having a large expansion coefficient, and joined to a manometer of small bore, is itself an exceedingly sensitive thermometer. It is clear that *osmotic effects* cannot be distinguished from the *"thermometer effects"* resulting from fluctuations of temperature. It is obvious, moreover, that *thermometer effects* in the cell can be *wholly* eliminated in one way only, and that is by maintaining in the bath a temperature so nearly constant that its fluctuations cease to produce a sensible effect upon the volume of the liquid enclosed in the cell. The ideal solution of this difficult problem would be a regulation so exact that not even the form of the mercury meniscus in the manometer could be sensibly affected by variations in the volume of the enclosed solution. This is the end to be striven for, although the task imposed is perhaps an impossible one. It must not be imagined that so high a degree of temperature regulation is unnecessary, and therefore absurd. On the contrary, even the variation in the form of the meniscus becomes a matter of importance whenever it is attempted to measure the osmotic pressure of concentrated solutions.

Since any pressure in the cell which exceeds the osmotic pressure of the solution necessarily forces a portion of the solvent out of the cell, while any under-pressure causes some of it to enter, it might be inferred that decided *thermometer effects* would become manifest only when the enclosed solution is subjected to rapid and large changes of temperature. But this is not the case. When the maximum osmotic pressure of a solution has once been developed in the cell, any subsequent readjustment between it and a thermometer effect due to an expansion or contraction of the solution is very slow; and especially so in cells in which considerable membrane has accumulated through long use, and in those also in which the membrane is of small area. In other words, when the osmotic pressure is nearly at a maximum, the trans-

ference of solvent in either direction through the membrane becomes very tardy. In this way is to be explained the fact, frequently observed, that the full recovery from a thermometer effect often requires several hours—nearly as much time, in fact, as did the development of maximum pressure after closing the cell. To give a concrete illustration of what is always observed when a change of temperature occurs in the bath, we will suppose that—after the maximum pressure has been developed in a cell and the height of the mercury in the manometer has remained practically constant for a long time, *e. g.*, an entire day— the temperature of the water in the bath undergoes a slight alteration. If the change is a rise in temperature, it is quickly followed by a rise of the mercury in the manometer, while a fall in temperature is as promptly followed by a descent of the mercury column. Moreover, to one who has not been duly impressed with the sensitiveness of the osmotic cell as a thermometer, the magnitude of the rise or fall of the mercury in the manometer—more precisely, the change in pressure—will seem out of all proportion to that of the change in the temperature of the solution. Now, although the solution may quickly regain its original temperature, the restoration of the original pressure will not be complete for several hours. The full recovery from the "*thermometer effect*" will, in fact, as previously stated, consume nearly as much time as did the development of the original maximum pressure. But the recovery may not be complete; for other changes of temperature may intervene before the requisite time for complete recovery has elapsed, introducing new complications, the nature and effect of which are too obvious to require explanation. An examination of our records will show that the pressure of the solution very rarely remains perfectly constant throughout an experiment. In nearly every case, slight fluctuations have been observed, even when the recorded temperatures of the bath have shown no variation. We have made a long and careful study of these ever-recurring fluctuations of pressure while the cells are in the bath, with a view to determining their cause or causes. A sufficient explanation of them

is to be found in the possible slight variations in the volume of the solution in the cell, combined, of course, with the well-known very slow passage of solvent through the membrane when pressure is nearly at a maximum; but there is another possible cause, namely, the breaking and mending of the membrane. The latter process, even if it exists, cannot be directly studied, hence we were obliged to content ourselves with ascertaining whether the fluctuations in question are *always accompanied by*, or *follow*, changes in the temperature of the bath. In every instance which has been brought under systematic observation, the variations in pressure—amounting perhaps only to changes in the form of the meniscus—have been identified as *thermometer effects*.

The recorded observations of pressures and temperatures in a given experiment are sometimes seemingly quite contradictory, as when the temperatures at the time of successive readings are found to be identical, while the pressures are different, or when the higher pressure is found to correspond to the lower of two temperatures. A little reflection, however, will show that both of these seemingly inconsistent situations are not only the possible, but frequently even the probable, results of *thermometer effects*.

Enough has been said to emphasize the necessity for the most careful regulation of temperature in the baths in which the cells are placed for the measurement of pressure. The need of such regulation does not, however, begin with the placing of the closed cells in the bath. It is a peculiarity of solutions that, when they are surrounded by a rigid semipermeable membrane, they are able—through a process of concentration or dilution—to accommodate their volume to any space which may be offered. This fact makes it imperatively necessary that the solutions, at the time of filling and closing the cells, shall have exactly the temperature at which the osmotic pressure is to be measured. Otherwise, the solutions are, to an unknown extent, more or less concentrated than was intended. It is to be remembered here that *concentration* means the numerical ratio of the molecules of the dissolved substance to those of the solvent, and not

the number of the former which is distributed through a unit
of space. Now, suppose that a cell is filled with a solution
having a lower temperature than that at which it is desired
to measure its osmotic pressure and that the cell is then closed
and placed in a bath of the required (higher) temperature.
The consequence is obvious. The capacity of the cell—that
is, the volume which the solution may eventually have—is
practically fixed at the time of closing, because the expansion
coefficient of the material of the cell walls is small, and the
initial mechanical pressure which is brought upon the solu-
tion is—or should be—nearly equal to the osmotic pressure,
so that the capacity of the cell can be but slightly increased
by any subsequent contraction in the volume of the gas in
the manometer. The first observed effect of the rising tem-
perature and nearly fixed volume of the solution is a pressure
considerably in excess of the true osmotic pressure. This
afterwards declines slowly, and finally becomes constant,
except as the equilibrium is subsequently disturbed by *ther-
mometer effects*. But the final pressure is still in excess of the
true osmotic pressure of the original solution, showing that
the solution in the cell has become more concentrated than it
was at the time of closing. In other words, the nearly fixed
volume of the solution has been maintained, in spite of *rising*
temperature, by the expulsion of a portion of the solvent.
Suppose, on the other hand, that the solution, at the time of
filling and closing the cell, has a higher temperature than that
of the bath in which its pressure is to be measured. The fixed
volume will then be maintained, in spite of *falling* tempera-
ture, by the acquisition of solvent from the outside, *i. e.*, by
dilution. The pressure will rise and finally become constant,
but it will always be less than the true osmotic pressure of
the original solution. The concentration and dilution which
take place when cells are filled with solutions having tem-
peratures different from those of the baths are permanent.
In this respect, they differ from the changes in concentra-
tion which attend *thermometer* effects. The latter are of a
temporary character.

Our first cells were set up, without any external protec-

tion, in a room which was subject to the usual variations of temperature. Some measures were taken, however, to moderate the extremes and to avoid very rapid changes of temperature. We were then under the impression that the passage of the solvent through the membrane is much more expeditious than it was afterwards found to be; and that, if the changes of temperature were moderately slow, the solutions would acquire or discharge the solvent with such facility that the observed changes of pressure could be interpreted as truly osmotic in character and due solely to changes in the concentration of the solutions in the cells. We were quickly undeceived. The fluctuations of pressure were far greater than could possibly be ascribed to changes in concentration. It then became clear that we had to deal with the osmotic cell as a *thermometer*, and that, in order to measure osmotic pressure with any degree of precision, the thermometric manifestations of the cell must be suppressed by the maintenance of nearly constant temperature in the bath. As a first step in this direction, the cells were placed in a wooden box with double walls. The spaces between the walls were filled with hair, and the box was both lined and covered with thick hair-felt. It was with this arrangement that the first series[1] of measurements of the pressure of cane sugar solutions was carried out. The fluctuations of temperature were much smaller and slower than before and the thermometer effects were correspondingly less pronounced. They were, nevertheless, still intolerably large. The greatest change in the temperature of a solution while in the box was $4°.48$; the smallest was $0°.75$; while the mean variation for the whole series of 24 determinations was $2°.03$. It should be stated, however, that some of the largest variations were due, in part, to the fact that at that time insufficient attention was given to the temperature of the solutions at the time of filling and closing the cells.

The next effort[2] to secure uniformity of temperature was of a much more elaborate character. A copper-lined rectan-

[1] This Journal, **34**, 1.
[2] *Ibid.*, **36**, 1.

gular tank, holding about 300 liters, was constructed and
symmetrically fixed in a wooden box of larger dimensions.
The considerable spaces between the two were filled with
hair, and a superstructure of equal width and depth, but only
three-fourths as long, was built over the top of the bath.
The front consisted of a plate-glass hinged window, while
the top (also hinged) and the remaining sides were double
walled and filled with hair. To further protect the enclosed
air space above the water against external conditions, the
glass front was completely covered with a thick hair pad.
This was divided into narrow strips, so that any part of the
interior space could be examined without uncovering any
large portion of the front. The remaining fourth of the top
of the bath—that portion which was not occupied by the
house—was covered with boards, on which rested the ma-
chinery employed in driving the pumps. There were two
pumps. One of them drew the water—at the rate of 20
liters per minute, if necessary—through a pipe lying on the
bottom, and delivered it at the top of the bath. The second
pump was employed in circulating the air in the enclosed
space through a system of pipes lying in the water below,
the purpose being to keep the two, if possible, at the same
temperature. The arrangement for stirring the water proved to
be entirely satisfactory, and it has never been abandoned or
even materially modified. That for maintaining the air in
the enclosed space at the temperature of the water was not
wholly effective, and though never discarded, in the later
work it has been supplemented by other devices which will
be described below.

As the laboratory was not heated at night, the bath was en-
closed by a structure—3.3 meters long, 2 meters in width,
and 2.6 meters in height—which consisted of a wooden frame-
work, covered on both sides with thick muslin. The cloth
upon the vertical walls was sized with gelatin, to render it
less pervious to air without interfering too greatly with the
light, while that upon the roof was both sized and painted.
The space within the enclosure was heated at night by an
electric stove which was controlled by means of a thermo-

stat. The larger room outside was also heated at night, but with a gas stove which was likewise under the control of an electric thermostat. The purpose of these heating devices, which were described in a former paper,[1] was not to maintain a constant temperature throughout a series of measurements, but merely to mitigate the extremes of temperature in the neighborhood of the bath. It was supposed that, with a bath so well protected by nonconducting materials and with a fairly uniform external temperature, the temperature of the large body of water within the bath would change so slowly that *thermometer effects* would be eliminated.

When the preparations just described were completed, a new series[2] of determinations of the osmotic pressure of cane sugar solutions was undertaken. The efficiency of the provisions which had been made for the maintenance of uniform temperature during the individual determinations may be judged by the following statements. The series in question consisted of 23 measurements of pressure. The greatest variation during any one experiment was $0°.95$; the smallest was $0°.00$; while the mean variation for the whole series was $0°.32$. The improvement on the temperature conditions under which the previous series of measurements had been made was very great and we were at that time convinced[3] that the results were but little influenced by *thermometer effects*. This opinion has since been revised, later and more systematic study of these phenomena having shown that much smaller fluctuations of temperature may sensibly vitiate the results.

While the variation in temperature during the time of any individual measurement was not seemingly large, the temperatures from experiment to experiment ranged from $20°.0$ to $24°.5$. We had not then, as we now have, the means for regulating bath temperature independently of external conditions, and we were, therefore, obliged to conform quite

closely to the room temperatures which prevailed during the daytime.

In another bath of identical construction and similarly protected against external conditions, a series[1] of determinations of the osmotic pressure of glucose solutions was carried out. Twenty-five measurements were made. In one experiment the variation in temperature amounted—through a neglect of one of the usual precautions— to $1°.3$. The greatest variation among the remaining 24 experiments was $0°.80$; the smallest was $0°.00$; and the mean variation for the whole series was $0°.31$. The highest average temperature at which any measurement was made was $26°.9$, and the lowest was $21°.9$.

During the following winter (1907) two series of measurements—one of cane sugar[2] and the other of glucose[3] solutions—were made at temperatures in the vicinity of $0°$. To prepare for the work at the lower temperatures, all available space in one of the baths—both in the water and in the air enclosure above—was filled with perforated galvanized iron ice boxes, and provision was made for the automatic discharge of the water which accumulated from the melting of the ice. In other respects the bath was not essentially changed. In the case of the cane sugar series, the highest mean temperature during any one of the 27 experiments was $0°.32$, while the lowest was $0°.14$. The greatest variation in temperature during any experiment was $0°.24$; the least was $0°.00$; and the mean variation for the whole series was $0°.10$. The regulation of temperature in the glucose series, which followed that of cane sugar, was slightly better. Here, the highest mean temperature during any one of the 20 experiments was $0°.28$; and the lowest, $0°.08$. The greatest variation in temperature during a single measurement was $0°.23$; the smallest, $0°.01$; while the mean fluctuation in temperature for the whole series was $0°.08$.

After the completion of the measurements of pressure in the vicinity of $0°$, the work entered upon a new phase

[1] This Journal, **37**, 324.
[2] *Ibid.*, **37**, 425.
[3] *Ibid.*, **37**, 558.

in respect to the regulation of temperature. It was desired
to determine the osmotic pressure of cane sugar and glu-
cose solutions at various temperatures between 0° and the
ordinary room temperatures. The agent which seemed to
lend itself most readily to this purpose was the hydrant water.
During a few weeks in the coldest season, its temperature
is ordinarily about 4°.0, while in midsummer, it may, for a
short time, exceed 25°. It was thought that by appropriately
choosing the season various fairly uniform temperatures could
be maintained in the bath for considerable periods by means
of running water, or, at least, that the fluctuations would not
necessarily exceed those which had been experienced while
measuring pressure at room temperature. Accordingly, one
of the baths was provided with a system of pipes through
which the hydrant water could be made to circulate at any
desired rate. A series of connected vertical brass pipes, hav-
ing a length, individually, of nearly a meter, an external diam-
eter of 20 mm., and an internal diameter of 16 mm., was ar-
ranged around the four interior walls of the bath. The dis-
tance between the pipes was 50 mm. Each pipe extended
from a point near the top of the air space to a depth of 36 cm.
under the water below, except for a short distance in front
of the window, where the pipes were shorter and did not en-
ter the water. A second series of connected horizontal pipes
—as long as the bath, and likewise 50 mm. apart—was sus-
pended close to the top of the air space. The section of pipes
in front of the window was removable, being connected, by
means of flexible hose couplings, on the one hand to the re-
mainder of the vertical system, and on the other to the hori-
zontal system above. Means were also provided for moving,
without opening the bath, the section of pipes in front of the
window whenever a pipe was found to obstruct the view
of a manometer. The circulating water passed continuously,
first through the system of vertical pipes, and then through
that of the horizontal pipes in the upper part of the air space.
The superficial area of all the pipes above the water was equal
to that of all the walls of the air space, including that of the
top; and its ratio to the surface of the submerged pipes was

about as 2 to 1. The water employed in regulating the temperature of the bath was brought in a large pipe directly from the basement, and there were no intervening outlets.

When the arrangement described above had been completed, it was attempted to measure the osmotic pressure of cane sugar solutions in the vicinity of $5°.0$;[1] but, as the series could not be finished before the beginning of April, it was necessary at times, especially in the latter part of the work, to cool the circulating water with ice. The efficiency of the device in regulating the temperature of the bath can be best judged by the following table in which the mean bath temperature and the extreme variations in temperature are given for each of the 20 experiments.

Table I.

Mean bath temperatures.	Extreme variation.	Mean bath temperatures.	Extreme variation.
$4°.84$	$0°.80$	$5°.03$	$0°.50$
$4°.93$	$0°.80$	$6°.05$	$0°.45$
$4°.58$	$0°.60$	$4°.35$	$0°.30$
$6°.05$	$0°.65$	$4°.55$	$0°.35$
$4°.50$	$0°.15$	$4°.48$	$0°.75$
$4°.50$	$0°.15$	$4°.33$	$0°.15$
$4°.48$	$0°.90$	$4°.33$	$0°.10$
$4°.51$	$0°.70$	$5°.23$	$0°.50$
$4°.34$	$0°.50$	$4°.60$	$0°.70$
$5°.23$	$0°.50$	$4°.32$	$0°.35$

It appears from the table that the maximum change in the temperature of the bath during any one experiment was $0°.9$; the minimum, $0°.1$; while the average variation for the whole series was $0°.5$. The control of temperature by means of running water had proved, in the first attempt, to be somewhat less satisfactory than that which had been secured at room temperature by the means previously described; and there could be no doubt that the results, like those of the earlier series, were vitiated to some extent by thermometer effects.

The idea of securing uniform temperatures by means of running water alone was abandoned, and it was decided to

maintain the water in the bath at a temperature slightly *above* that of the water circulating in the pipes. The heating, according to the plan developed along this line, was accomplished and controlled by submerged electric stoves and thermostats. The beneficial results of the new scheme were immediately apparent. Four new series[1] of measurements, comprising 80 determinations of osmotic pressure, have been finished since it was put in operation. In 53 of these, there was no sensible change in temperature while the cells were in the bath; in 17 experiments, it amounted to $0°.1$ or less; in 7, the variation was $0°.2$ or less; while in three it did not exceed $0°.3$. The plan was not immediately perfected, hence fluctuations of bath temperature occurred more frequently, and were larger, in the earlier work. The details of the new arrangement were gradually improved and finally brought into such a highly satisfactory state, in nearly every respect, that, throughout the last of the four series, there was not any sensible variation in bath temperature.

The account of the present improved methods of regulating temperature would be incomplete without a sketch of the earlier attempts to maintain an equality of temperature in the water of the bath and in the enclosed air space above. It is manifestly desirable, though it is not absolutely necessary, that the solution in the cell, which is submerged in the water, and the gas in the manometer, which is in the enclosed air space, shall have the same temperature. There are, however, certain very obvious difficulties in the way of securing and maintaining this condition. The water, by virtue of its enormous capacity for the absorption of heat without much change in temperature, is only slowly affected by external conditions, while the enclosed air is very sensitive to them. Moreover, it is impracticable, in a structure which, like the enclosure over the water bath, must be frequently opened, to make the joints gas-tight. Hence the air within is constantly escaping, while the outer air is as constantly entering the enclosed space.

At the outset, the walls surrounding the air space were

[1] This Journal, **39**, 667; **40**, 1, 194, and 325.

made as nearly tight and as completely nonconducting as pos-
sible, and the hinged front and top were made to close against
rubber weather strips; and during a measurement, the joints
were covered externally with surgeon's adhesive tape. But
the provision from which most was expected was the forced
circulation of the air through pipes lying in the water. Four
series[1] of measurements were carried out before introducing
any decided improvements in the original scheme for keep-
ing a uniform temperature in the two sections of the bath.
The following table will show for each series the number of
readings made, the greatest and least observed difference
between the temperature of the water and that of the air,
and the average of all the differences.

Table II.

Series.	Number of readings.	Greatest difference.	Least difference.	Average of all differences.
I.	100	$2°.50$	$0°.00$	$0°.53$
II.	90	$1°.90$	$0°.00$	$0°.44$
III.	137	$1°.65$	$0°.08$	$0°.68$
IV.	83	$0°.91$	$0°.30$	$0°.60$

The success of the attempt to maintain the equality of tem-
peratures in question is best judged by the averages in the
last column. The "greatest" differences are of little signifi-
cance, as they were usually due in large measure to the neces-
sity, which occasionally arose, of opening the bath during an
experiment; in other words, to temporary causes. Series I.
and II. were carried out at room temperature, while III. and
IV. were made at temperatures close to $0°$. This will ex-
plain why the averages of the second pair are higher than
those of the first, since the difficulty of maintaining the en-
closed air at the temperature of the water in the bath obviously
increases with the difference between the temperature of the
latter and that of the external air.

The circulating system of pipes for hydrant water pre-
viously mentioned was next introduced into the bath for the
purpose of securing several intermediate temperatures, and

an attempt was made to measure the osmotic pressure of cane sugar solutions in the vicinity of $5°.0$. But the temperature of the hydrant water soon rose above $5°.0$, and it was frequently necessary to employ small quantities of ice, both in the water and in the enclosed air space. This could be done fairly successfully in the case of the water, but the introduction, even of small quantities, of ice into the air space often produced considerable and irregular changes of temperature. As regards the maintenance of equal temperatures in the two divisions of the bath, *i. e.*, in the water and in the air space, this series is to be regarded as less satisfactory than any which preceded or followed it, though in some other, more essential respects, it was better than any previous one. The following tabular statement presents the number of readings, the greatest and the least observed differences between the temperature of the water and that of the enclosed air, and the average of all the differences:

Table III.

Series.	Number of readings.	Greatest difference.	Least difference.	Average of all differences.
V.	79	$5°.05$	$0°.63$	$1°.47$

Later, a number of improvements were gradually introduced with a view to securing greater constancy of temperature in the water, and at the same time greater uniformity of temperature in the two divisions of the bath. The character of these improvements will be made clear in the latter part of this paper. For the present, it is only necessary to show, by means of the following table, how far they have contributed toward the second object. The statement concerns the last four series of measurements, *i. e.*, those which have been made since the submerged electric stove and thermostat mentioned above were first introduced into the water of the bath. Here again, the results should be judged, not by the "greatest" differences, which are of an accidental and temporary character, but by the means of all the observed differences in temperature:

Table IV.

Series.	Number of readings.	Greatest difference.	Least difference.	Average of all differences.
VI.	63	1°.40	0°.20	0°.68
VII.	56	1°.80	0°.00	0°.67
VIII.	67	1°.50	0°.00	0°.49
IX.	80	0°.60	0°.00	0°.12

In the last series (IX.), the average of all differences was only 0°.12, and this is a fair measure of the agreement between the temperature of the water and that of the air above it which we are able to maintain with our present arrangements.

The introduction into the bath of a system of pipes through which the hydrant water was made to circulate, and, later, of electric heaters and thermostats which were submerged in the rapidly moving water surrounding the pipes, led, in a short time, to the elaboration of a general scheme for water bath regulation. The central idea of the system may be stated as follows: *If the water in any bath is made to pass rapidly (1) over a continuously cooled surface, then (2) over a heated one which is more efficient, but under the control of a thermostat, and (3) again over the cooling surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water.* The principle is a general one and provides for the maintenance of any temperature between 0° and the boiling point of water. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid either in the work of the cooling surface or in that of the heating surface, according as its temperature is lower or higher than that which is being maintained in the bath.

We shall now attempt to show how the principle stated above has been utilized in our most recent work upon osmotic pressure; and, first of all, we shall describe, not the bath in which the measurements are made, but that in which the solu-
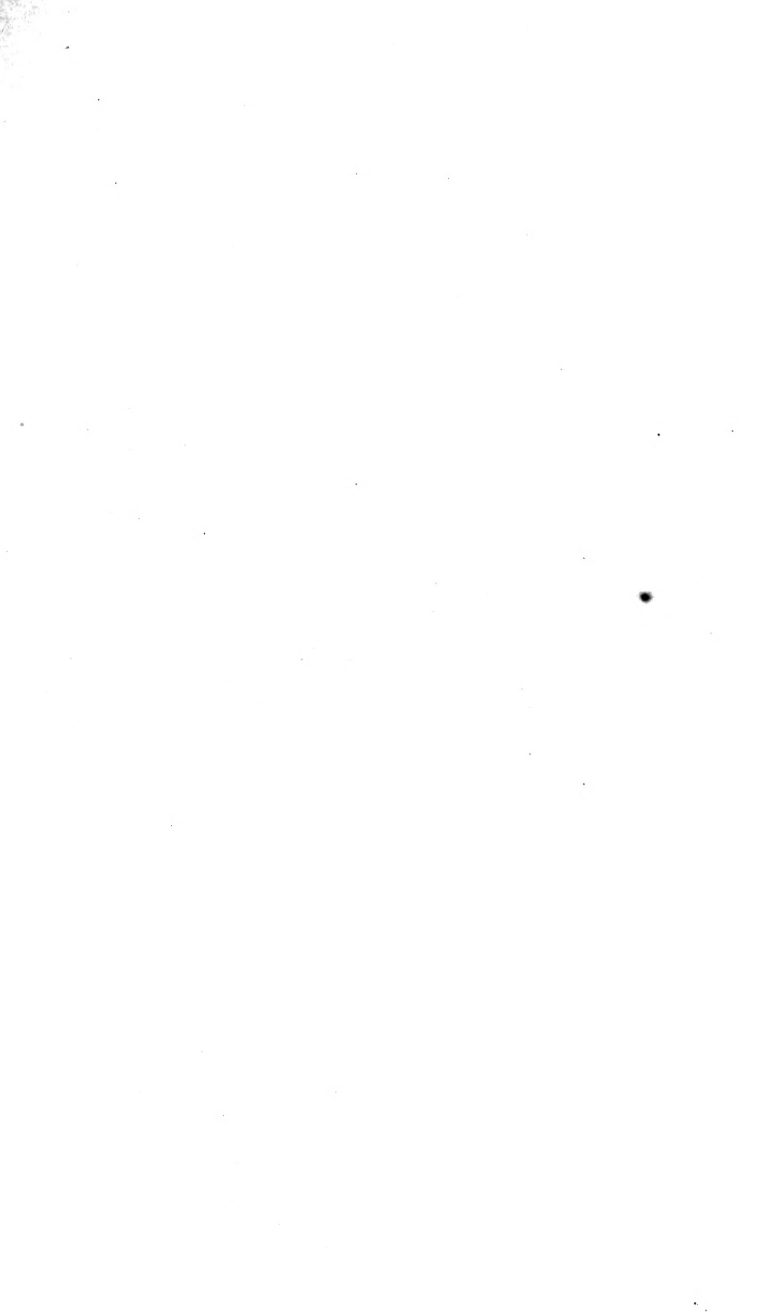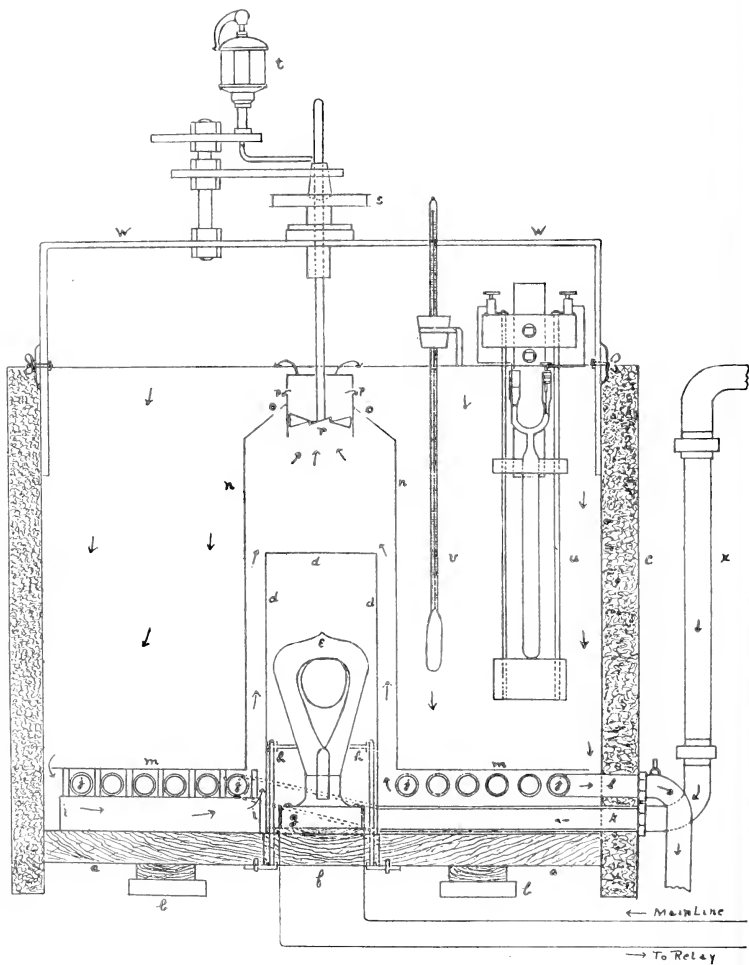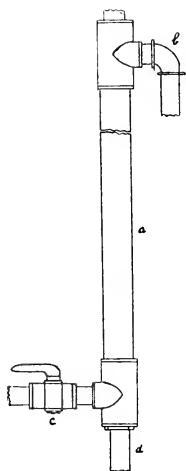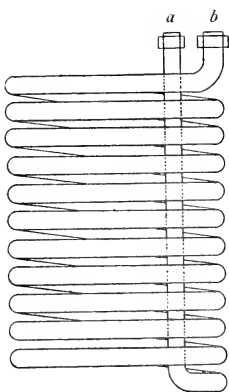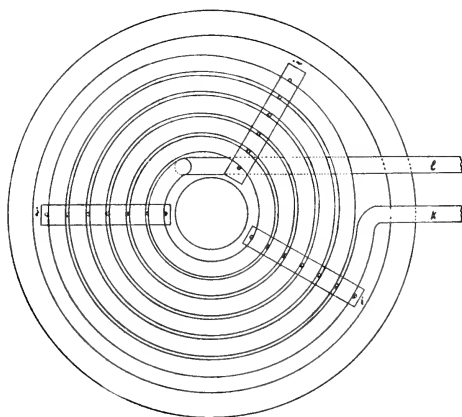
Fig. 1.

Fig. III.

Fig. IV.

Fig. II.

tions are brought to the required temperature before filling the cells, and in which, also, the cells are kept before and after a measurement of pressure. We may also state that in the laboratory the bath about to be described has generally superseded, in one form or another, all other devices for maintaining constant temperature between 0° and 100°.

Fig. I. represents a cross section of a galvanized iron bath holding about 60 liters. It rests upon the wooden base *a a*, which is raised above the table by the blocks and rubber pieces *b b*, and is surrounded by the thick hair pad *c c*. Inverted over a hole in the center, and riveted and soldered to the bottom of the bath, is the cylinder *d d d*, which serves as a receptacle for the lamp *e*, or any other suitable kind of electrical heating device. The hole in the wooden base *a a* is slightly larger than that in the bottom of the bath, and into this is fitted the block *f*, on which is fastened the lamp base *g* and the lamp guard *h h*. The lamp block is held in its place by buttons screwed to the bottom of the wooden base.

Resting upon the framework *i i* (Fig. I.) and *i i i* (Fig. II.) is the continuous block-tin pipe *j j j i*, through which the hydrant water circulates. This furnishes the "cooling surface" previously referred to. The running water enters the bath at *k* and leaves it at *l*. The course of the water in the pipe, after entering the bath, is continuously horizontal or upward—never downward. This arrangement is necessary in order to prevent the lodgment of air in any part of the pipe. The plan of the continuous tin pipe and of the frame on which it rests is seen in Fig. II. The successive coils of the pipe (six in number) are separated by the pegs seen in Figs. I. and II., and on these rests the galvanized iron disc *m m*. The hood *n n* shuts down tightly over a flange on the disc *m m*, and is secured in its place by means of set screws directed towards *d d*. The form of the hood will be clear from the figure, and it is necessary only to call attention to the pin holes, for the escape of air, at *o o*, and to the larger holes at *p p*, through which a portion of the water raised by the propeller *r* escapes into the outer bath.

The propeller r is revolved at any required speed by a smooth porpoise-hide belt, six mm. in width, which is passed around the pulley s, and over the pulley of a small motor located at some distance from the bath. To prevent vibration, a long belt, supported at intervals by loose pulleys, is used. The wearing parts of the machinery are lubricated from the oiler t. The thermostat is seen at u, and the thermometer at v. The supports for both are clamped to the rim of the bath, as is also the adjustable support $w\,w$ for the propeller and its accessories.

It is quite essential that the hydrant water flowing through the pipe in the bath shall be under a constant pressure; otherwise, much water and heat are necessarily wasted. The arrangement by which the constant pressure is secured is shown in Fig. III. It consists of a large standpipe a, with an overflow b near the top. The water from the tap enters at the bottom and passes to the bath through c, where the flow is controlled by a stop-cock. The circulating water is thus brought under an invariable pressure, and it is possible to regulate the quantity passing through the bath with great exactness and for long periods.

It frequently happens that the temperature of the hydrant water is higher than that at which it is desired to maintain the bath. In such cases, the section of pipe x, Fig. I., is removed and replaced by another leading to the coil of block-tin pipe seen in Fig. IV. The water enters the coil at a (Fig. IV.) and passes out of it at b into the bath. To cool the hydrant water before it enters the bath, the large and well-protected box in which the coil is located is filled with ice. With the aid of the coil, surrounded by ice, it is practicable to maintain quite low temperatures in the warmest weather.

It remains to explain the electrical arrangements for heating the water in the bath. It is important that the metallic surface $d\,d\,d$ (Fig. I.), over which the water passes in its upward course through the hood, shall be quickly heated and readily cooled; hence all unnecessary material in the space heated by the stove is to be avoided, and the stove itself should be of the lightest kind. For this reason, lamps have
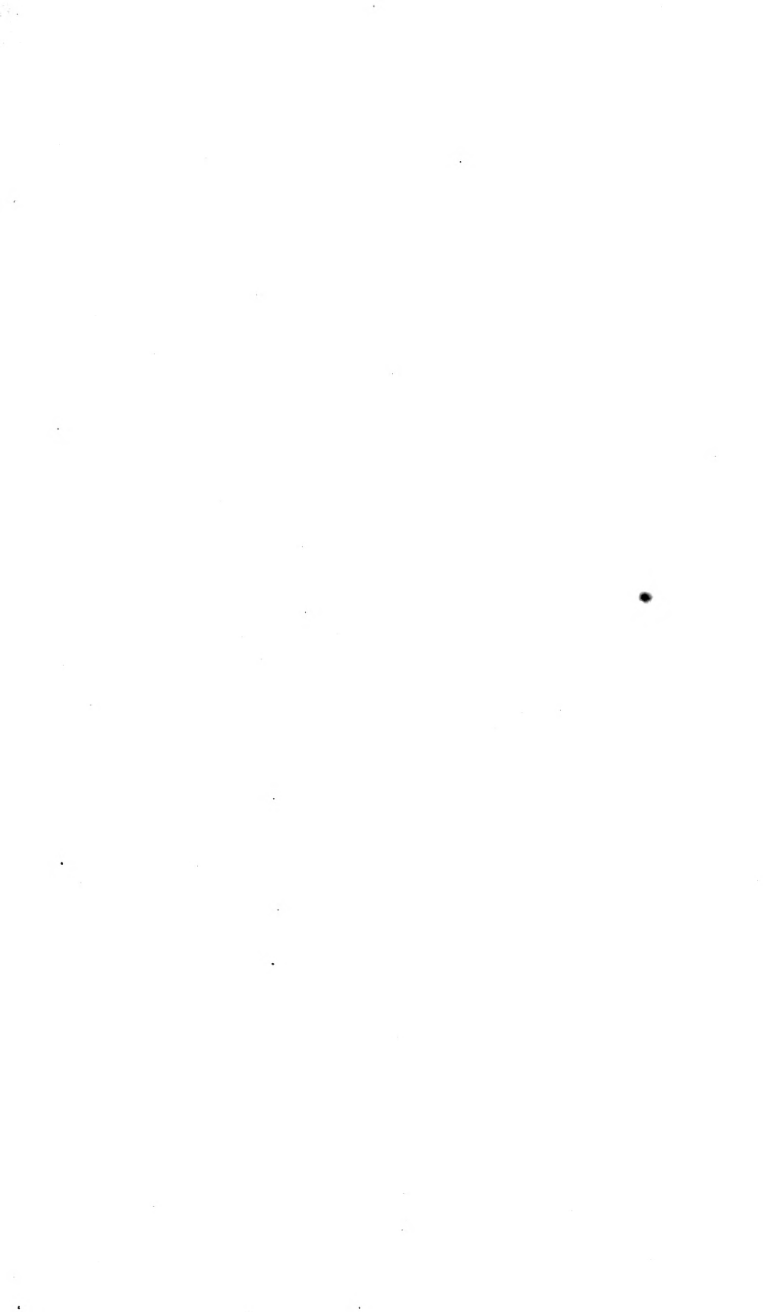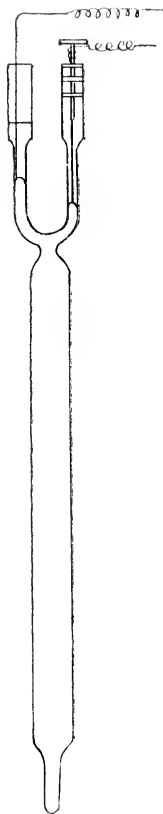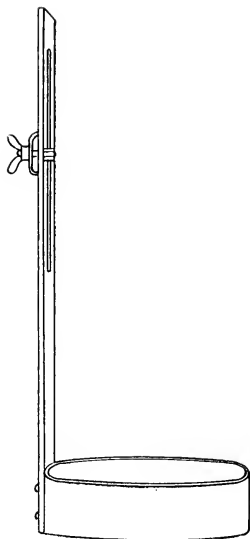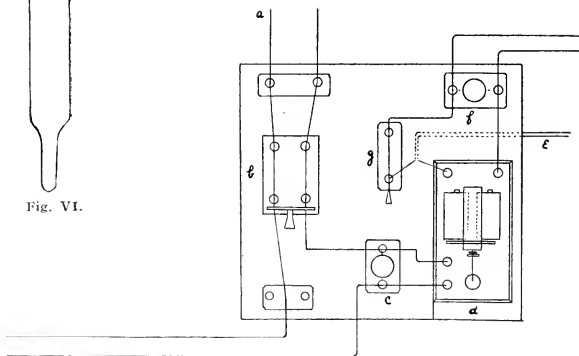
Fig. VI.

Fig. VII.

Fig. V.

been preferred to any other variety of electrical heating device. Another great advantage to be gained by the use of lamps is the ease with which, by the selection of lamps with different candle power, the capacity of the stove is suited to the work to be done, *i. e.*, to the temperature to be maintained in the bath.

The arrangement for the regulation of the heater (*e*, Fig. I.) by the thermostat (*u*, Fig. I.) is shown in Fig. V. The main line *a* passes through the switch *b* to the heater *e*, Fig. I. On the return, it crosses one end of the lamp socket *c* and enters the relay *d*. From thence it crosses the other end of the lamp socket and passes through the switch *b*. It will be seen that, whenever the circuit is broken at the relay, the lamp in *c* is thrown into series with the heater *e*, Fig. I., cutting down the current more or less according to the resistance in *c*. The voltage of the current employed is 120, and the resistance in *c* is usually a 240 volt, 16 candle power lamp. The lamp in *c* serves another important purpose. It spans the break in the relay and prevents sparking between the platinum contact points.

The line *e* (Fig. V.) from the single storage cell which operates the relay, after passing through the coils of the instrument crosses one end of the lamp socket *f*, and then passes on to the thermostat *u*, Fig. I. On its return, it crosses the other end of the lamp socket *f*, and passes back to the battery through the switch *g*. The lamp in *f* prevents sparking in the thermostat just as that in *c* suppresses it in the relay. The resistance in *f* should be about 200 ohms, or that of the cold filament of a 16 candle power, 75 volt lamp.

The thermostat is shown separately in Fig. VI. The tube containing the mercury is made larger or smaller, according to the degree of sensitiveness which is required of the instrument. It is also drawn out at the lower end into a smaller tube, which may be broken off and afterwards resealed if it becomes necessary to remove the mercury and cleanse the glass. The narrow tubes in the upper part of the instrument are also varied in diameter according to the requirements of the work. The instrument is filled with mercury until it enters the wi-

dened portion of the two tubes at the top. The end of a platinum wire is buried to a considerable depth in the mercury in one tube, and on the top of the mercury a quantity of dry shellac is placed. The shellac is melted and diminished pressure is applied at the other outlet until the mercury, followed by the molten shellac, recedes well into the narrower portion of the tube, when the shellac is allowed to cool and solidify. The other tube at the top is provided with an adjustable platinum wire, the function of which is sufficiently obvious.

A thermostat of the form just described has the advantage that all of the mercury in the instrument can be submerged in the water of the bath, while the arrangement for adjustment remains above the surface of the water. But the range of temperatures through which it can be used with a fixed quantity of mercury is small. That is, the quantity of mercury must be regulated with reference to the temperature which is to be maintained. This, however, gives very little trouble. If a thermostat is to be employed to maintain a bath at some particular temperature, *e. g.*, $25°$, it is plunged —after removing the adjusting screw—into a bath having a slightly higher temperature, and whatever mercury ascends into the wider portions of the tube is removed by means of a very fine pipette. On the other hand, if the mercury recedes too far into the narrow tube, more is added.

We mentioned in an earlier paper[1] the method of suppressing sparking in the thermostats and relays by spanning the spark gap by a resistance bearing a definite ratio to the voltage of the current. The device has proved to be a very useful one, and it is employed in all of our numerous arrangements for the regulation of temperature. It has been found, however, that the desired end, *i. e.*, the suppression of sparking, is much more readily accomplished if the necessary resistance is spread over a large surface. Accordingly, in the large permanent bath, the spark gaps of the thermostat are spanned, not by lamps, but by porcelain tubes which were evenly painted with a mixture of bolted clay, finely pulverized graphite, and a little soap, until the proper resistance

[1] THIS JOURNAL, **36**, 14.

had been secured.   This is the same mixture which was recommended in a former paper[1] for the preparation of heating surfaces of various kinds, and it is especially adapted to the purpose of spreading any required resistance uniformly over any area of surface.

Notwithstanding the suppression of all visible sparking, the mercury in the narrow tube of the thermostat becomes somewhat stiff, after a time, and the instrument begins to respond less promptly to minute changes in temperature. Whenever a symptom of this kind is detected, the thermostat is placed in a bath of higher temperature, and the mercury which rises into the enlarged portion of the tube is removed and replaced by fresh metal.

It may not be out of place to mention here a new kind of thermostat of extreme sensitiveness, in which mercury contact is avoided.   We shall only explain the principle on which it is constructed because some of the mechanical details have not yet been perfected.   The principle in question is that of a balance, in which two glass bulbs connected by a nearly capillary tube play the part of the beam.   One of the bulbs is closed, except for the opening into the glass tube, while the other bulb has attached to it a short open tube.   The closed bulb and the connecting tube are filled with mercury, and a quantity of mercury equal to that in the closed bulb is put into the slightly more capacious open one.   It will be seen that if an arrangement of this kind is placed upon a knife edge in such a position that the center of gravity is slightly below the point of suspension, we shall have a sensitive temperature balance; for any change in the volume of the mercury, in effect, transfers a portion of the metal from one end of the beam to the other, and the difference in the weight of the two ends, which is thus produced, is double that of the mercury transferred.   The instrument is provided with means for adjusting the distance between the point of suspension and the center of gravity, according to the degree of sensitiveness required, and also for equalizing the weight of the two arms of the beam.   The circuit is opened and

[1] This Journal, **32**, 93.

closed by means of the "pointer." Such an instrument must, of course, be adequately protected against currents of air or water.

Fig. VII. represents the support for flasks, etc., which is used in the bath. It is clamped to the rim of the bath, and, as will be seen from the figure, it can be depressed to any required depth in the water. The bottom is perforated to permit the rapid passage of water. Each bath of the size represented in Fig. I. will accommodate five such supports in addition to the thermostat and thermometer.

The use of the bath is very simple. The thermostat is adjusted to close the circuit at the temperature at which the bath is to be maintained. The bath is brought nearly to that temperature by means of hot water, or ice, or by passing a current of hydrant water through the coiled pipe in the bottom. The flow of hydrant water—cooled, if necessary, by first passing it through the ice coils (Fig. IV.)—is then so regulated that it will very slowly lower the temperature of the circulating water in the bath. The rate of the lowering need not exceed $0°.25$ per hour, and it should be, for reasons of economy, as small as it is possible to make it. The lamp which is employed as a heater is selected with reference to the temperature to be maintained. It is only necessary that it shall be able, by burning all the time, to raise the temperature of the bath somewhat faster than the running hydrant water is able to lower it. The thermostat will then permit the lamp to burn only as much of the time as is necessary to maintain the temperature for which the instrument is set.

The water, as it reaches the top of the hood, after passing over the heating surface, is symmetrically distributed towards all sides of the bath, giving a uniformity of temperature throughout the bath which is very satisfactory.

The maintenance of any temperature from a little above $0°$ to that of the room can be readily accomplished by means of the hydrant water, with or without ice. If, however, a temperature above that of the room is to be maintained, the flow of the hydrant water is cut off. The outer surface of the bath and the free surface of the water then become the

"cooled" surface, and the bath works on precisely the same principle as when hydrant water is made to circulate through the tin pipe in the bottom. If a temperature above 50° is to be maintained, the consumption of electrical energy becomes expensive in large baths, and it is well to accomplish a portion of the heating by other means. This is done in various ways, the simplest of which is to remove the wooden base and place a gas stove under the bath, taking care so to regulate the quantity of burning gas that the stove *alone* cannot raise the temperature of the bath to the required height. It is only the remainder of the work which is then accomplished by the electrical heater. Another method of economizing electrical energy, when high temperatures are to be maintained, is to cause hot water to circulate through the pipe in the bottom of the bath, using for the purpose a device constructed on the principle which is employed in house heating by hot water. Here again, the work which the auxiliary heater is allowed to do must be less than the required maximum, so that the final regulation of temperature may always fall to the electrical devices.

It may be of interest to learn how closely bath temperatures may be regulated by the means here described. We can say, in general, that the variations can not ordinarily be detected on thermometers which are graduated to tenths of a degree and which can be read to hundredths. In the case of one bath of 60 liters capacity, in which a temperature of 25° was being maintained, we took the trouble to ascertain definitely the range of temperature within which the thermostat would open and close, or close and again open the lamp circuit. It was found to be 0°.002.

The same principles are employed in regulating the 300-liter baths in which the measurements of osmotic pressure are made. It will, therefore, be necessary only to mention certain peculiarities in the arrangements for this part of the work. The system of pipes which was first introduced into the bath for the purpose of circulating the hydrant water proved to be unsatisfactory in one way. The pipes, as explained in the earlier part of this paper, were placed *vertically*

around the sides of the bath, with the lower ends under the water and the upper ends in the air space above. The obvious purpose of the arrangement was to maintain an equality of temperature in the two sections of the bath. The difficulty which arose was one which should have been foreseen. The gas which was expelled from the circulating hydrant water, in consequence of rising temperature, collected in the upper ends of the tubes to such an extent that it was frequently necessary to "flush out" the whole system; and this brought about changes in the temperature of the bath which could not be tolerated. Accordingly, the vertical pipes were removed, and in their place was introduced a circulating system which will be briefly described. Supported on an open framework near the bottom of the bath is a series of connected horizontal brass pipes with an aggregate length of 10 meters. This collection of pipes is the analogue of the coiled block-tin pipe in the bottom of the bath previously described. The hydrant water enters it, from the pressure regulator, at the lowest point and passes through the succession of pipes, always in a horizontal or upward direction, thence through a vertical pipe to the air space above. The vertical pipe here connects with a second system of horizontal pipes, placed one above another, which is fixed to the walls of the air space; and the water, after circulating through this, enters a third system of horizontal pipes which is suspended from the top of the bath. There is no opportunity for the lodgment of gas in any part of the course taken by the water, hence it is practicable to regulate the flow with considerable exactness. If necessary, the hydrant water is cooled, before entering the bath, by passing it through a coil of pipe surrounded by ice. The slowly circulating water, while passing through the pipes lying in the bottom of the bath, is warmed nearly to the temperature of the bath water, and it may not, on that account, be able, while passing through the upper portion of the system, to keep the temperature of the air space low enough; hence provision is made for reinforcing the stream with an additional quantity of cold water while it is running through the upper part of the bath.

In the large bath, as in the smaller one represented in Fig. I., the water is pumped first over the cooled surface, *i. e.*, over the pipes near the bottom, and then over the heated surface. Each of the baths is provided with two stoves, either one of which may be operated independently of the other, though both are under the control of the same thermostat. Fig. VIII. shows one of the stoves enclosed in a galvanized iron tube. The stoves are located in the end of the bath which is not covered by the superstructure, and they are, therefore, accessible from the outside.

The arrangements as described are satisfactory in respect to the maintenance of constant temperatures in the lower section of the bath, *i. e.*, in the water in which the osmotic cells are placed for a measurement of pressure, but they were found to be insufficient to maintain the same temperatures in the upper section, *i. e.*, in the air space in which the upper ends of the manometers are located. Even the rapid pumping of the air in this section through pipes lying in the water, and the introduction of a small fan—propelled from the outside—to agitate the air, did not fully neutralize the effect of external conditions. It was therefore decided to bring these external conditions under better control by making the necessary provisions for keeping, outside of the bath, approximately the same temperature as we were endeavoring to maintain on the inside.

The bath, as stated in an earlier part of this paper, is located in a small room, 3.3 meters in length, 2 meters in width, and 2.6 meters in height. It was this space which was to be automatically heated or cooled, according to the demands of the work going on inside the bath. We shall first describe the cooling device. It consists of a series of galvanized iron pipes, having a total length of 100 meters, through which the hydrant water—cooled by ice, if necessary—may be made to flow at any required rate. One-half of the pipe, namely, 50 meters, is suspended from the top of the room in parallel lengths equal to the length of the room itself. These pipes have a diameter of about 50 mm. and present, therefore, a large cooling surface. The remainder of the pipe (50 meters)

is smaller (25 mm. in diameter), and is cut into 2 meter lengths, which are compactly arranged in a large ice box. The water enters the ice box directly from the main supply, and, after passing through the series of short pipes in the box, it ascends through a vertical pipe to the system of symmetrically distributed large ones in the top of the room.

There are two varieties of heating devices in use. One of these consists of two small electric stoves, which are situated outside the bath but are controlled by a thermostat *within* the air space. The other heating arrangement is a gas stove controlled by a thermostat which is located on the *outside* of the bath. The purpose of the gas stove is simply to economize electrical energy, and it is used only when a considerable supply of heat is necessary. It is never allowed to furnish all the heat required, and that it may not do so, its thermostat is set for one or two degrees below the temperature which is to be maintained in the bath. The final regulation of the temperature of the little room is thus always left to the electric stoves, which, being under the control of a thermostat within the enclosed space, can burn only so much as is necessary to keep the temperature of the space up to that of the water in the bath. The air in the room is kept in constant circulation by a motor fan which is located with a view to keeping the temperature of all parts of the room as uniform as possible.

With these facilities for cooling and heating, we are now able to maintain a variety of constant bath temperatures without much regard to the season of the year; nevertheless, it is advisable, on economical grounds, to do the work at low temperatures in winter and that at higher temperatures in summer. It will be seen that the problem to be solved is the same in every case, namely, to regulate the cooling devices so as to produce, both within and without the bath, a temperature somewhat below the one at which the work is to be done, and then to leave the differences to the automatic heating devices.

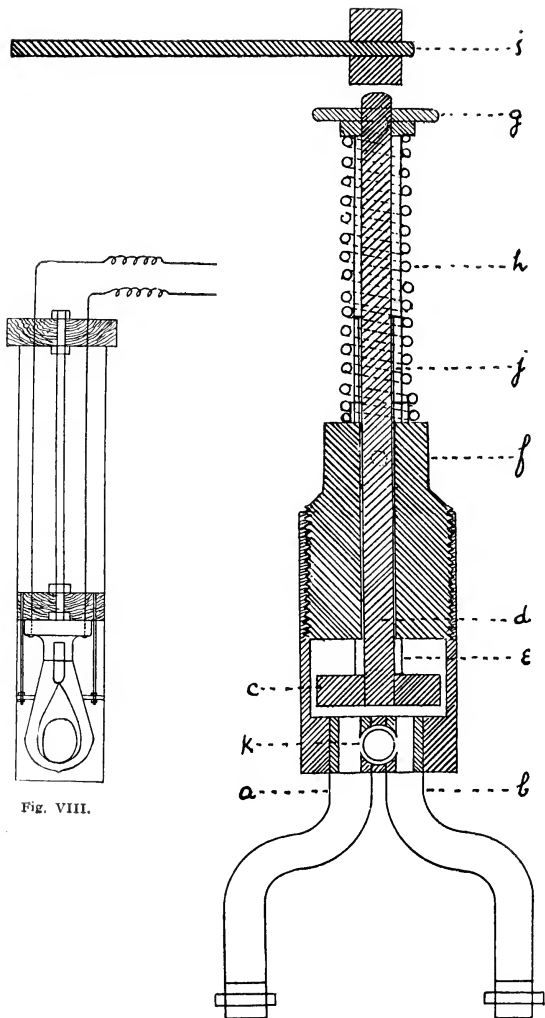The gas regulator which is used with the stove is perhaps

Fig. VIII.

Fig. IX.

worthy of a description. In a former paper[1] we gave an account of a gas regulator in which the flow of the gas is controlled by an iron ball, which is raised into place and dropped again by the closing and opening of the circuit of an electro-magnet. The instrument, when correctly made, was a satisfactory one except in one particular. It was found very difficult to obtain perfectly spherical balls of sufficiently pure and soft iron. All of those which were used became, after a time, permanently magnetized to such an extent as to render the regulators unreliable. They were therefore abandoned for the form of regulator which is shown in Fig. IX. It is made entirely of brass and is connected directly—*i. e.*, without the intervention of rubber tubing—on the one side to the gas supply pipe, and on the other, to a metal tube leading to the stove. The two pipes *a* and *b* through which the gas flows are closed and opened by the disc *c*. Above the disc, upon the rod *d*, to which it is attached, is the soft rubber ring *e*. The distance through which the disc *c* may move is regulated by the threaded plug *f*, through which the rod *d* passes. Above the plug *f* is the spiral spring *h*, the strength of which can be regulated by the nut *g*. The spring raises the disc *c* and permits the gas to pass from pipe to pipe, as long as the hammer *i* is raised; but when the hammer descends, the disc is driven down upon the open ends of the pipes, shutting off the gas. The hammer is worked by an electro-magnet, which is under the control of a thermostat, and it remains down, stopping the flow of gas, as long as the circuit is closed. To prevent a possible escape of gas into the room, a thin, very flexible rubber tube *j* is slipped over the rod *d* and over a short metal tube projecting from the upper end of *f*. The two pipes communicate also through the hole *k* and the amount of gas which may take this course between the pipes is regulated by the screw *l*.

[1] THIS JOURNAL, **36**, 18.

ON THE RELATIVE EASE OF ADDITION IN THE AL-KENE GROUP.

[FIRST PAPER ON THE LAWS OF ADDITION IN ORGANIC CHEMISTRY.]

By Arthur Michael and Roger F. Brunel.

In organic chemistry numerous attempts have been made to formulate empirical laws to apply to addition phenomena. Markonikoff,[1] who first noted a regularity in the addition of halogen acids to unsaturated hydrocarbons, laid down the rule that the halogen in such cases goes to the carbon joined to fewer hydrogen atoms, *i. e.*, to the one most under the influence of other carbon atoms. A few years later it was shown by Saytzeff[2] that this rule was not general even for alkenes, since it was found that in the addition of hydriodic acid to unsymmetrical ethylmethylethylene the halogen unites with the unsaturated carbon which, from the Markonikoff point of view, is less under the influence of other carbon atoms,[3] and Linnemann[4] showed that it was not valid for unsaturated organic acids, as in the union of halhydric acids with acrylic acid the halogen unites with the methylene and not, in accordance with the principle involved in the Markonikoff rule, with the methine group.[5] In 1887 one of us[6] showed that a general law of addition, not only comprehending the various classes of unsaturated organic derivatives but connecting the course of the process with the structure of the substances, could be based on the "positive-negative" hypothesis. It is safe to say, however, that an empirical law cannot be formulated to which exceptions will not be found, and we shall give here a brief outline of the subsequent development[7] of the "posi-

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[1] Ann. Chem. (Liebig), **153**, 256 (1870).

[2] *Ibid.*, **179**, 296 (1875).

[3] Compare Michael: J. prakt. Chem., N. F., **60**, 348 (1899).

[4] Ann. Chem. (Liebig), **163**, 96 (1872).

[5] Later Hemilian (*Ibid.*, **174**, 326) and Fittig and his pupils (*Ibid.*, **188**, 42; **195**, 56) endeavored to prove that with other acids of this series α-halogen derivatives are formed, but Erlenmeyer, sen. (Ber. d. chem. Ges., **13**, 394) and Michael and Freer (J. prakt. Chem., N. F., **40**, 96) showed that β-substituted acids are really formed.

[6] Michael: J. prakt. Chem., N. F., **37**, 524.

[7] Michael: *Ibid.*, **60**, 341-351, 443-470; **68**, 499; Ber. d. chem. Ges., **39**, 2139, 2143, 2157.

tive-negative" law of addition, which is universal since it is founded on the principle underlying all chemical phenomena, *i. e.*, the law of entropy.

The second law of thermodynamics demands that all spontaneously occurring chemical changes shall be accompanied by an increase in the entropy of the system. Furthermore, we know that where several courses are possible for a reaction the *tendency* is to follow that by which the greatest increase in entropy will result; while, the nearer together the entropy changes in the different directions lie, the more nearly equal become the amounts of the corresponding products obtained[1]— a more fundamental and general statement of the partition principle first suggested by Thomsen[2] in connection with his investigations on the avidity of acids. To establish a more direct connection in the change of any chemical system between the change in entropy and the constitution of the compounds that may be formed, we may start from the assumption that the more nearly complete the neutralization of the chemical forces in the new chemical system, the greater will be the entropy.[3] It follows from such a relation that the tendency of any unsaturated organic substance, in passing over into a more saturated derivative, is to give rise to a substance whose structure or configuration represents the maximum chemical neutralization of the atoms. This neutralization principle has been expressed by one of us as follows: "In any chemical reaction the total energy of the atoms involved is the more completely converted into bound energy and heat, the more nearly the chemical forces in these atoms are able to neutralize each other."[4] In an organic substance which represents a very complete state of intramolecular neutralization, the energy of each atom is largely expended through direct union or through space in holding in combination the other atoms of the molecule, and the portion of the energy so expended is here designated as *bound chemical* energy. In as far as the chemical forces in the molecule are

[1] Michael: J. prakt. Chem., N. F., **60**, 340; Ber. d. chem. Ges., **39**, 2138.
[2] Pogg. Ann., **138**, 497.
[3] Michael: J. prakt. Chem., N. F., **68**, 489.
[4] Michael: *Ibid.*, N. F., **60**, 292; Ber. d. chem. Ges., **38**, 23.

not so neutralized, some of the atoms will still be able to exert attraction toward such other atoms as they have an affinity for in the same or other molecules, and this portion of the energy, not used directly or indirectly through union with the rest of the atoms of the molecule, is designated as *free*[1] *chemical* energy. When the chemical forces of opposite character[2] in the molecule are nearly equal, neither the molecule as a whole nor any of its atoms can exert much attraction towards other molecules. There can be but little free chemical energy present in such a molecule and the substance will be comparatively stable and, in general, chemically inactive.[3]

It is now necessary to see what connection there is between these principles and the velocity of chemical reactions. It is assumed that the first step in every chemical reaction is the formation of an intermediate "Kekulé double molecule."[4] The velocity with which the reaction takes place will depend largely on two factors: first, the attractive force between the reacting molecules, which determines the ease with which the double molecule will be formed, and depends on the amount and nature of the free *chemical* energy present;[5] second, on the increase in entropy brought about by the reaction, which is a large factor in determining the tendency of the double molecule to rearrange to give the resulting substances. The fact that in the cases where different products may be formed the reaction does not always lead at once to the formation of those which would represent the highest degree of entropy

[1] The terms free and bound *chemical* energy, as here used, are not to be confused with the terms free and bound energy as used in physical chemistry, with which they are not identical.

[2] These forces of opposite chemical character are often designated as positive and negative. These terms are confusing, since they bring to mind some sort of electrical conception. Although they sometimes coincide with the electrochemical character of the atoms or radicals in question, there is no inherent connection with these, the terms being merely relative, and used to designate kinds of chemical energy which act differently from each other.

[3] For further details regarding the application of these principles see Michael: J. prakt. Chem., N. F., **68**, 488; THIS JOURNAL, **39**, 1; Ber. d. chem. Ges., **39**, 2139-2163; **41**, 2907; Ann. Chem. (Liebig), **363**, 21-106; **364**, 64.

[4] Kekulé: Ann. Chem. (Liebig), **106**, 141. Michael: Ber. d. chem. Ges., **34**, 4028; **39**, 2140; THIS JOURNAL, **39**, 3.

[5] The two factors that permit a chemical change, *i. e.*, free chemical energy and chemical affinity, have together been designated chemical potential (see Michael: Ann. Chem. (Liebig), **363**, 21).

of the system must be attributed to intramolecular resistance of some sort, due sometimes to the difficulty in overcoming the bound *chemical* energy existing between certain atoms. The *chemical* potential of the atoms is not always sufficiently strong to overcome this intramolecular resistance to the formation of the structure or configuration representing the maximum entropy of the system.[1]

A typical example of the application of these principles to organic chemistry is to be found in the addition of halogen acids to unsaturated hydrocarbons. Here free *chemical* energy is always present in considerable amount in the hydrocarbon, the question being whether it is of such a nature as to attract the hydrogen and halogen of the addendum. Furthermore, when the addition leads to the formation of isomeric products, the breaking down of an alkene-halogen acid double molecule involves no rearrangement of atoms already joined, except the separation of hydrogen and halogen, which is the same for both of the possible isomers, so that the relative amounts of the products may be assumed to be dependent only on the entropy of the two reactions.[2] The question as to whether such an addition will take place, and as to which of two possible isomers will be formed (or, if both, in what ratio) will depend on the possible extent of neutralization of both the hydrogen and halogen in the molecules of the addition products that may be formed.

The idea, first suggested by van't Hoff,[3] that the influence which two atoms in a molecule exert on each other is to be divided into two parts—first, direct, acting through direct union or through space; second, indirect, exerted through the intermediate atoms—has been further developed[4] and shown

[1] See Michael and Bunge: Ber. d. chem. Ges., **41**, 2908.

[2] While it cannot be stated at present just how near the relative amounts of isomers formed in the addition reactions here under consideration come to those demanded by the entropy of the reactions, there is certainly an approximate agreement (see Michael: This Journal, **39**, 6; Ber. d. chem. Ges., **39**, 2140-2163; J. prakt. Chem., N. F., **68**, 499). It is apparent that we can consider from the above point of view only reactions where the states of aggregation of the systems before and after the chemical change are so similar that the entropy factors arising from these causes may be eliminated.

[3] Ansichten, I., 284; II., 252.

[4] Michael: J. prakt. Chem., N. F., **60**, 331; Ber. d. chem. Ges., **39**, 2138-2157 and 2780-2790; **40**, 140.

to be of great importance in enabling us to understand organic reactions. If in an aliphatic compound with normal chain a certain carbon atom be designated by the figure 1, our present knowledge of the mutual influence between this atom and others in the molecule is best expressed by the following scale, the numbers indicating degree of removal from the atom in question and the strength of the influence decreasing in the order given:[1]

$$2-3-5-6-4-7-(9-10-11)-8.$$

It is to be strongly emphasized that the effect of an atom not far removed, *i. e.*, in position 2 or 3, whether it is direct or, if indirect, lessened by the interference of only one atom, is far greater than that of any similar atom less closely connected; and that in the case of atoms farther removed the influence must be largely direct, *i. e.*, spatial. By numbering the atoms as above and summing up the influences acting on the two unsaturated carbon atoms of an alkene hydrocarbon, we can ascertain the relative degree of neutralization of the halogen and hydrogen atoms of the adding acid in the two isomeric addition products which may be formed. We shall then know more or less closely the relative increases in entropy which would result from the formation of the two isomeric compounds, and this, in connection with the principle of partition, will determine the relative amounts formed,[2] it being assumed, as stated above, that here the intramolecular resistances are equal in each case; while if the increase in entropy is much greater for one than for the other, the latter will not be produced in appreciable quantity, although we must assume that in all cases both possible isomers are formed.[3]

How structural changes in the compounds concerned may affect the relative amounts of isomers formed has been already

[1] J. prakt. Chem., N. F., **60**, 335.

[2] This has been shown experimentally in the addition of hydriodic acid to 2-hexene (Michael and Hartman: Ber. d. chem. Ges., **39**, 2149) and of water to 2-hexine (Michael: *Ibid.*, **39**, 2143).

[3] This was proven in the case of addition of hydriodic acid to propylene (see Michael and Leighton: J. prakt. Chem., N. F., **60**, 466).

discussed and examined experimentally by one of us.[1] The point of primary importance in this paper is the relative additive power of different alkenes.

To consider the case most generally from a theoretical standpoint, let us represent any compound containing an ethylene grouping (C : C) by the formula $\overset{\displaystyle X}{\overset{\textstyle \diagup\diagdown}{C : C}}$,[2] including under X all the rest of the molecule, and assuming for the present that its effect on the two carbon atoms is practically the same. We may imagine in the first place that X is of such a nature that while the resulting power of the unsaturated carbons to unite with hydrogen is great they have little capacity to combine with halogen. The entropy change, when the second stage of the addition takes place, that is, when the double molecule changes over into an ordinary molecule, is the sum of three quantities: the change involved in separating hydrogen from chlorine (negative) and those involved in the union of these with the two carbon atoms (positive). If the last two together are greater than the first, the addition may take place, for the neutralization will be greater after it does; otherwise, it could not spontaneously occur. In the case above described, the energy of chlorine would be so much less completely neutralized in combination with carbon than in hydrochloric acid that a greater degree of entropy is represented by $\overset{\displaystyle X}{\overset{\textstyle \diagup\diagdown}{C = C}} + HCl$ than by $X\diagdown\!\!\begin{array}{c} C\!\!-\!\!H \\ | \\ C\!\!-\!\!Cl \end{array}$. In such a case

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[1] Michael: J. prakt. Chem., N. F., **60**, 345-351 and 445; **68**, 499; Ber. d. chem. Ges., **39**, 2141 and 2143. Exceptions to the Markonikoff rule have from time to time been found and some of these have already been discussed by one of us and explained according to the principles stated above. One recent very interesting instance may be mentioned here. Delacre (Centralb., **1906**, I., 1233) found that hydriodic acid adds to tertiary butylethylene to give a primary, instead of the expected secondary, derivative. This exception to the Markonikoff rule is attributed to "unexplained influences." The nine hydrogen atoms of the tertiary butyl group are, however, in the 4-position to the β and the 5-position to the α unsaturated carbon atom, and the much greater influence of atoms in the latter place could leave no other result to be expected than the union of the halogen to a very considerable extent with the α carbon atom. Since, however, the determining forces here are all those of atoms not directly connected with the unsaturated carbons, the product of the addition should contain also the secondary iodide in appreciable quantity (see Ber. d. chem. Ges., **39**, 2141).

[2] This is not intended to represent a ring compound.

spontaneous decomposition of the latter compound would be possible, if the attraction between hydrogen and chlorine were sufficient to overcome their union with the carbon atoms.

But we may alter the character of X so that the affinity of carbon for chlorine will increase. This will be the result if X contains atoms which themselves have an affinity for chlorine, in the present case hydrogen atoms, but this will at the same time decrease the tendency of the carbon to unite with hydrogen.[1] Nevertheless, addition may now occur, *i. e.*, such addition would be accompanied by increase of entropy.[2]

The tendency to add will increase as we continue to alter the character of X in the same direction. This will hold, however, only to a certain point, for we are decreasing the power of the unsaturated carbons to unite with hydrogen, so that after a point of relatively great additive power is passed, we shall again approach a point where addition cannot take place spontaneously, this time because, while the affinity for the chlorine is great, the union of carbon with the hydrogen of the adding acid will represent so slight a degree of neutralization that a higher degree of entropy will again be found in the system $\overset{\displaystyle X}{\overset{\displaystyle \diagup\diagdown}{C = C}}$ + HCl. Here, again, the compound $X\left\langle\begin{matrix} C-H \\ | \\ C-Cl \end{matrix}\right.$, if formed under certain conditions, might decompose spontaneously at ordinary temperature.

In the alkene series X consists of carbon and hydrogen atoms. Since additional carbon atoms have much less effect on those already present than atoms of a different character,

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[1] Carbon in itself has an affinity for hydrogen and for the halogens and other nonmetallic atoms as well, but the degree of this affinity can be considerably affected by other atoms present in the molecule. Carbon and hydrogen are chemically remarkably plastic, *i. e.*, their affinity relations are very sensitive to the influence of other atoms (van't Hoff: Ansichten über organ. Chem., I., 280; II., 242; Michael: J. prakt. Chem., N. F., **60**, 325). With increasing influence of hydrogen on an unsaturated carbon, its chemical character tends to become more and more like that of more metallic elements. Such changes must therefore increase the affinity of the carbon for halogen, but decrease it for hydrogen (see J. prakt. Chem., N. F., **60**, 290 and 326; Ber. d. chem. Ges., **39**, 2192).

[2] This would not, of course, mean that it would in general occur, but with the alkenes, since large amounts of free *chemical* energy are always present, we may safely assume that it will occur if this energy is of the required character.

i. e., the hydrogen atoms, we need take only the latter into consideration in the present case. On account of the affinity of hydrogen for chlorine we should expect the presence of hydrogen atoms in the molecule to increase the power of carbon to combine with the chlorine so that, in successive members of the series, the latter is constantly becoming more completely neutralized. But toward the hydrogen of the hydrochloric acid, the affinity of the carbon must be lessened by the influence of an increasing number of hydrogen atoms already present in the molecule. Data for the first three members of the aliphatic series have long been available, showing that the additive power toward acids increases as we go up the series, but for the reasons given above it could be stated with certainty that at some point a maximum[1] must be reached, beyond which the neutralization of the hydrogen would be so incomplete that the additive power would become less and less, and, if the series could be continued far enough, might reach zero.

This occurrence of a maximum in additive power may be considered the second part of the fundamental law governing addition phenomena, and will always appear when the addendum consists of hydrogen and a relatively negative atom or group.[2] Examples of this relationship are not wanting in both inorganic and organic chemistry.

In the case of the ammonium and phosphonium compounds, etc., the failure to take this principle into account has caused considerable confusion between *tendency to dissociate* and *basicity* of the radicals.[3] Ammonium chloride is a fairly stable substance, but if the nitrogen be successively replaced by phosphorus, arsenic, and antimony, compounds result which, with increasing *metallic* character of the element, so greatly decrease in stability that phosphonium chloride exists only at $-30°$ and the corresponding arsenic and antimony compounds have never been isolated. This does not,

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[1] It is possible that two alkene hydrocarbons with practically the same additive power exist, but our present knowledge does not tend to confirm this view.

[2] See Michael: Ber. d. chem. Ges., **38**, 28. Michael and Cobb: Ann. Chem. (Liebig), **363**, 68.

[3] See Michael and Leighton: Ber. d. chem. Ges., **39**, 2792.

however, justify the conclusion that the AsH_4 and SbH_4 are less basic than the PH_4 and NH_4 radicals, for the stability of these chlorides does not depend on their basicity, but on the question whether a greater degree of neutralization is found in the union of hydrogen with chlorine, or in that of hydrogen and chlorine with the group XH_3. As we substitute the more metallic elements for nitrogen, the ability to neutralize hydrogen decreases, and one of the above elements will give to the radical XH_3 a certain affinity for both hydrogen and chlorine, which will cause a maximum degree of stability in the compound XH_4Cl. That element is nitrogen. Substitution of phosphorus, arsenic, or antimony produces a greater tendency to dissociation, but there is no reason to doubt that in stable derivatives of the four radicals (XH_4) those of SbH_4 would show greater power to neutralize chlorine, that is, be more basic than any of the others.[1]

An interesting illustration of the above law in organic chemistry is found in Bredig's[2] research on the conductivities of alkylammonium bases in aqueous solution. Bredig showed that the value of K increases considerably in passing from a mono- to a dialkylamine, but that from the latter to a trialkylamine an almost equally marked decrease occurs. He concluded from these results that the dialkylamines are stronger bases than either the mono- or trialkyl compounds. It is extremely improbable that such an irregularity in the degree of dissociation of the substituted ammonium hydroxides would occur, but it is more likely that they would all be dissociated to a very considerable extent and that the degree of dissociation would increase slightly with the introduction of each additional alkyl group. On the other hand, there is every reason to believe that the conductivity of the alkylamines in aqueous solution depends largely on the proportion of the amine in combination with water as alkylammonium hydroxide, so that Bredig's results only show

[1] The tetramethylhydroxy derivatives of these four elements are known and; although they are all strong bases, there can be no doubt that tetramethylstibonium hydroxide is the strongest and tetramethylammonium hydroxide the weakest base of the series.

[2] Z. physik. Chem., **13**, 289 (1894).

that the dialkylamines unite to a greater extent with water, than the mono- and trialkyl derivatives, *i. e.*, the dialkylammonium hydroxides are more stable than the mono- or trialkylammonium compounds under the conditions of the experiments.[1] Here we notice a similar change in the stability relations. The resultant of the affinity of the compounds $C_nH_{2n+1}NH_2$ for hydrogen and hydroxyl increases with the introduction of a second alkyl radical, but a further repetition of the change decreases that for hydrogen so greatly that a decrease in the stability of the additive product results.[2]

In regard to the additive power of the lower members of the ethylene series the following experiments were already described in the literature. Berthelot[3] showed that ethylene is hardly affected by being heated one hundred hours at 100° with saturated aqueous hydrochloric acid, while propylene is absorbed in seventy hours under the same conditions. Butlerow[4] found that ethylene dissolves readily in concentrated sulphuric acid only at 160°, propylene is acted on at room temperature, while isobutene[5] is absorbed in a short time at room temperature by 50 per cent acid. These facts leave little doubt as to the relative additive power of the three hydrocarbons in question, but later experiments[6] were more satisfactory, as they included a larger number of alkenes and were carried out with dry hydrochloric and hydrobromic acids at the same time and under exactly the same conditions. It was found that ethylene unites less readily than propylene and this less readily than *n*-butene, and, in accordance with the theory,[7] the difference in the velocities between the first is considerably less than between the last-named hydrocarbons. Furthermore, of the isomeric butenes, isobutene unites much

[1] A similar relation has been proven experimentally with the trialkylammonium cyanides. See Michael and Hibbert: Ann. Chem. (Liebig), **364**, 64.

[2] Conductivity measurements of the substituted ammonias in aqueous solution do not represent the relations between the relative basicities of such substances, but those of the relative stability of the corresponding ammonium hydroxides in aqueous solution. An experimental research on this subject will be published later.—A. M.

[3] Compt. rend., **54**, 1350.

[4] Ann. Chem. (Liebig), **180**, 246 (1875).

[5] Ber. d. chem. Ges., **6**, 561 (1873).

[6] Michael: J. prakt. Chem., N. F., **60**, 372 (1899).

[7] *Ibid.*, 373.

more readily than pseudobutene, and the latter somewhat more so than *n*-butene, so that, of the alkenes of the first four series, the additive power is considerably the greatest for isobutene.

That there exists a maximum degree of additive power, with a decrease in the higher members of the alkene series, appeared probable from the observations of Butlerow[1] that diisobutylene adds halogen acids only slowly, and of Kondakow[2] that with hydrochloric acid even heating with the fuming acid in sealed tubes to 100° does not entirely complete the reaction, while the products easily give up the halogen acid. Furthermore, according to Butlerow,[3] triisobutylene seems to add with still greater difficulty and, although it adds bromine readily, the product, as we should expect in accordance with the small affinity for hydrogen, easily gives up hydrobromic acid.

With the object of finding where the maximum of additive power is reached, isobutene, trimethylethylene, tetramethylethylene, and diisobutylene have been investigated. Most of the experiments were carried out with aqueous sulphuric acid, but halogen[4] and phosphoric acids were also used. The expected decrease appeared between isobutene and trimethylethylene, the former being dissolved by aqueous acids in from one-fourth to one-third of the time required by the latter. In passing to tetramethylethylene and diisobutylene the difference in each case is greater than between the first two, as is shown by the figures given below.

Thus, of all the alkenes hitherto examined, isobutene (I.) shows the greatest additive power,[5] and in this compound there exists

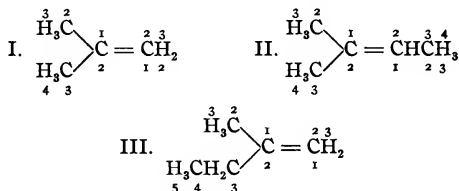[1] Ann. Chem. (Liebig), **189**, 51 (1877).

[2] J. prakt. Chem., N. F., **54**, 449 (1896).

[3] Ber. d. chem. Ges., **12**, 1483 (1879).

[4] With halogen acids the solutions were dilute enough so that the hydrocarbons added, not acid, but water, giving carbinol. We have investigated this phenomenon and it will form the subject of the second paper of this series.

[5] As far as is known, every alkene is capable of uniting with the usual inorganic addenda, so that additive power coincides here with relative rate in the velocity of the additions. Recalling what has been said above, the velocity of addition with different alkenes may depend on: first, the amount and character of the free *chemical* energy of the unsaturated hydrocarbons; and, second, the increase of entropy brought about by the reaction. It is not possible at present to say what part each factor plays, but that is for the present case unnecessary, since here the two influences work in the same direction. That substance which, through its chemical energy, has the greatest attraction for the two parts of the addendum is the one which will best neutralize their energy by combination.

the greatest difference of polarity between the unsaturated car-
bon atoms. According to the scale of relative influences given

$$\text{I.} \quad \overset{3\ \ 2}{\text{H}_3\text{C}} \!\!\diagdown \overset{1}{\underset{\underset{4\ \ 3}{\text{H}_3\text{C}}\diagup{}_2}{\text{C}}} = \overset{2\ 3}{\underset{1\ 2}{\text{C}\text{H}_2}} \qquad\qquad \text{II.} \quad \overset{3\ \ 2}{\text{H}_3\text{C}} \!\!\diagdown \overset{1}{\underset{\underset{4\ \ 3}{\text{H}_3\text{C}}\diagup{}_2}{\text{C}}} = \overset{2\ 3}{\underset{1}{\text{C}\text{H}}}\overset{3\ 4}{\underset{2\ 3}{\text{C}\text{H}_3}}$$

$$\text{III.} \quad \overset{3\ \ 2}{\text{H}_3\text{C}} \!\!\diagdown \overset{1}{\underset{\underset{5\ \ 4\ \ 3}{\text{H}_3\text{CH}_2\text{C}}\diagup{}_2}{\text{C}}} = \overset{2\ 3}{\underset{1}{\text{C}\text{H}_2}}$$

above, the hydrogen of the two methyl groups is in such a
position as to increase to the greatest possible extent the af-
finity of the β unsaturated carbon for halogen ($\overset{2\ 3}{\text{CH}_3}$), and to
decrease least that of the α carbon for hydrogen ($\overset{3\ 4}{\text{CH}_3}$). In
trimethylethylene (II.) the additional methyl group is in a
position where the hydrogen will affect strongly the carbon
with which the hydrogen of the adding acid is to unite ($\overset{2\ 3}{\text{CH}_3}$),
and only weakly that to which the halogen goes ($\overset{3\ 4}{\text{CH}_3}$).

In 1877, LeBel[1] described a method for separating the amyl-
enes by means of the differences in their capacity to unite with
hydrochloric acid, and also reached the conclusion that only
those homologues of ethylene containing the group : CRR′
(that is, those that form tertiary halides in the addition) are
attacked readily in the cold. Thus trimethylethylene (II.) and
unsymmetrical methylethylethylene (III.) unite more readily
than the other amylenes. The difference now found between
the additive power of isobutene and trimethylethylene shows
that in the series containing 5 carbon atoms the number of
hydrogen atoms is already sufficiently great to cause a
decrease, and we are now able to account for the difference
among the amylenes. Addition takes place readily in this
series only where *one* of the unsaturated carbons is joined to
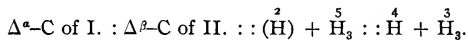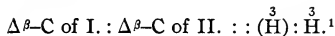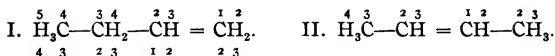two alkyl groups, so that while its attraction for the halogen

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[1] Bull. Soc. Chim., **28**, 460. Wischnegradsky (Ann. Chem. (Liebig), **190**, 332)
subsequently used dilute sulphuric acid to separate the amylenes, as only those that
can pass over into the tertiary carbinol dissolve readily.

is strongly marked, that of the other unsaturated carbon for hydrogen is not correspondingly decreased. The additive power of unsymmetrical methylethylethylene (III.) should be greater than that of trimethylethylene (II.), since the latter adds less easily than isobutene (I.), and the introduction into isobutene of 3 hydrogen atoms in position 5 (relatively to the unsaturated carbon that unites with the hydrogen of the addendum) must decrease the additive power less than when they are introduced in position 3. Methylethylethylene (III.) and trimethylethylene (II.), respectively, are thus related to isobutene (I.).[1]

From the above discussion it is clear that isobutene should possess greater additive power than the other butenes. This would, indeed, be considered very probable merely from the fact that, in adding, it alone forms tertiary derivatives; for the high heat of formation of the tertiary halides and carbinols as compared with the secondary, and of the latter as compared with the primary derivatives[2], is an indication, according to the neutralization principle (p. 119), of the relative condition of intramolecular neutralization in these compounds, and thus of the relative increase in entropy. If we designate the atoms in normal and pseudobutene as above and sum up the influences of the hydrogen, first, on the carbon atoms with which the negative group or atom of the addendum will unite, and second, on the carbon atoms to which the hydrogen will add, omitting such atoms as have exactly or nearly the same value for both, and using parentheses to indicate those hydrogen atoms which are joined directly to unsaturated carbon atoms, as they must have a decidedly less positive effect than those united with saturated carbon, we have the following result:

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[1] Whether unsymmetrical methylethylethylene or isobutene possesses the greatest additive power in the alkene series can only be determined by experiment, and we shall try to decide the question in this way.

[2] The rule governing these values has been stated (Michael: J. prakt. Chem., N. F., **68**, 499) as follows: "The heats of formation of aliphatic organic isomers which have a negative organic nucleus in common is proportional to the total influence, *i. e.*, direct as well as indirect, of the positive hydrocarbon radicals on this negative nucleus." Thus, propionic aldehyde and acetone have in common the negative carbonyl nucleus, which, however, is joined directly to the two methyl groups only in the latter substance. This, therefore, has the greater heat of formation.

I. $\overset{5}{H_3}\overset{4}{C}—\overset{3}{C}\overset{4}{H_2}—\overset{2}{C}\overset{3}{H} = \overset{1}{C}\overset{2}{H_2}$.   II. $\overset{4}{H_3}\overset{3}{C}—\overset{2}{C}\overset{3}{H} = \overset{1}{C}\overset{2}{H}—\overset{2}{C}\overset{3}{H_3}$.

Δ^β–C of I. : Δ^β–C of II. : : $(\overset{3}{H})$: $\overset{3}{H}$.[1]

Δ^a–C of I. : Δ^β–C of II. : : $(\overset{2}{H}) + \overset{5}{H_3}$: : $\overset{4}{H} + \overset{3}{H_3}$.

It is apparent that the influence of hydrogen is somewhat greater on the Δ^β–C of pseudobutene (II.) than on the Δ^β–C of normal butene (I.), which means that the Δ^β–C of pseudobutene has a somewhat greater affinity for the negative component of the addendum than the Δ^β–C of normal butene; while the Δ^a–C of normal butene, since it is less under the influence of hydrogen than the Δ^β–C of pseudobutene, *may* have a somewhat greater attraction for the hydrogen of the addendum. Obviously it is impossible to determine theoretically the relative values of the velocity of addition to these butenes, although it could safely be concluded that the difference between them could not be very great. Preliminary experiments[2] had already indicated that the additive power of the pseudo compound is somewhat greater, and according to the experiments described below, in which dilute sulphuric acid was used as additive reagent, it is nearly twice as great as that of *n*-butene,[3] while the ratio with iso- and pseudobutene is 60–80 : 1.

The hydrocarbons used in this reasearch, with the exception of diisobutylene, were prepared from the iodides by treatment with alcoholic potash. The comparatively low temperature employed makes this method the least likely to cause isomerization. With normal and isobutyl iodides only one alkene is possible, but from the secondary deriva-

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[1] In conformity with von Baeyer's suggestion (Ann. Chem. (Liebig), **245**, 112) the capital "Delta" denotes unsaturation: *i. e.*, Δ^β–C is the carbon of the CH-group in I. and II.

[2] Michael: J. prakt. Chem., N. F., **60**, 372.

[3] It is assumed here that ordinary pseudobutene (compare Wislicenus, Talbot, and Henze: Ann. Chem. (Liebig), **313**, 228) represents the fumaroid form, which must have a considerably smaller additive power than the maleinoid derivative. When we start from those acetylene derivatives that give stereomeric isomers, we introduce obviously a greater complication in the addition processes, and some facts are known that seem not in accordance with the law of addition. It will be shown later that such apparent contradictions disappear when the reactions are considered from the point of view of the energy relations of the stereomeric products (see THIS JOURNAL, **39**, 1).

tive either 1-butene or 2-butene may result. In 2-iodo-
butane (CH_3—CH_2—CHI—CH_3) the hydrogen of the methyl
is more firmly joined to carbon than that in the methylene
group, owing to the direct union of the latter with the second
methyl.[1] Moreover, with the formation of 2-butene, the
maximum entropy of the reaction is at once realized, as that
hydrocarbon has a greater heat of formation than 1-butene,
owing to the more intimate influences of the hydrogen atoms
on the negative nucleus (CH:CH). However, from the
theoretical standpoint, some 1-butene should be formed
and our experiments, though not conclusive, indicate that
this is the case. From similar reasons, dehydration of ethyl-
dimethylcarbinol, or treatment of the corresponding iodide with
alkali, should give chiefly trimethylethylene; still some un-
symmetrical methylethylethylene should be formed, and
Wagner[2] has shown that this is the case (7 per cent) with the
product from the iodide.

No method of determining with any degree of accuracy
the composition of a mixture of butenes has yet been described.
Scheschukow[3] attempted such a determination of the iso
and pseudo compounds, based on the supposition that of
the two addition products formed with hydriodic acid the
tertiary (from isobutene) is decomposed completely, the
secondary not at all, by boiling water. Ipatiew and Ogon-
owsky[4] used the same methods with the bromides, but Ipa-
tiew[5] more recently has shown that under these conditions
pseudobutyl iodide is hydrolyzed to a considerable extent,
and it is therefore doubtful if the bromide method can give
even approximately accurate results. Konowoloff[6] liquefied
the mixture of gases and absorbed the isobutene by sulphuric
acid mixed with an equal weight of water. But Butlerow's
statement[7] that under these conditions the pseudobutene is
slowly absorbed indicates that this method cannot be accurate.

[1] Michael: J. prakt. Chem., N. F., **60**, 353.
[2] Ber. d. chem. Ges., **21**, 1235.
[3] *Ibid.*, **19**, R. 544.
[4] *Ibid.*, **36**, 1988 (1903).
[5] *Ibid.*, **40**, 1829 (1907).
[6] *Ibid.*, **13**, 2395 (1882).
[7] *Ibid.*, **9**, 77 (1878).

As the ratio of the isomeric butenes formed in different reactions is of interest in connection with the principle of partition, it would be of value to have a method of analyzing these mixtures, and we have partially succeeded in attaining this object by a modification of the methods previously used. The absorption apparatus described by Butlerow,[1] consisting of a glass tower filled with glass beads over which sulphuric acid trickles, was first tried but could not be made to give good results. The method found to be most satisfactory consisted in the use of Hempel gas pipettes with sulphuric acid of proper concentration. A sharp separation is not possible since acid sufficiently strong to dissolve one of the isomers at a rate great enough to be of service acts appreciably on at least one of the others, but such a concentration can be chosen that results correct to within a few per cent can be obtained. For use in the separation of isobutene from 2-butene, three parts of acid, by weight, are diluted with two parts of water. To analyze a mixture of 1- and 2-butenes, seven parts of acid are diluted with two parts of water, but the results here are much less accurate than in the first case.

<div align="center">EXPERIMENTAL PART.</div>

<div align="center">*Preparation of the Butenes.*</div>

Isobutene.—This was prepared by the method of Butlerow,[2] from isobutyl iodide, alcoholic potassium hydroxide, and an excess of solid alkali. The yield was 75–80 per cent. The iodide was prepared from the alcohol by means of the red, as well as the yellow, phosphorus, and iodine. The former method gave a slightly larger yield, the latter a purer product. Hydriodic acid and the alcohol give a still purer product, but the yield calculated from the amount of iodine used, is not so good.

2-Butene.—This was prepared like isobutene.[3] Eighteen grams of iodide, 36 grams of alcoholic potassium hydroxide (3 parts alcohol to 1 part hydroxide), and 15 grams solid hydroxide gave two liters of gas, *i. e.*, 87 per cent of the calcu-

[1] Z. Chem., **13**, 238 (1870).
[2] *Ibid.*, **13**, 238 and 544 (1870); Ber. d. chem. Ges., **3**, 622 (1871).
[3] De Luynes: Ann. Chem. (Liebig), **132**, 275 (1864).

lated amount. Secondary butyl alcohol was prepared according to the directions of Sabatier,[1] by passing a mixture of methylethyl ketone and hydrogen over reduced nickel. From the product the alcohol is easily obtained pure by fractionation.

1-Butene.—This was prepared like the other isomers. The yield was poor (only 24 per cent), due, as Lieben and Rossi[2] showed, in large part, to the formation of ethylbutyl ether. In the hope of improving the method by the use of a different solvent, some preliminary experiments were made on the action of alkali on ethyl iodide in acetone, glycerol, and isobutyl alcohol. Lieben and Rossi[3] state that when ethyl iodide is heated with alcoholic potash only a slight amount of ethylene is formed. We obtained ethylene in considerable quantity only when isobutyl alcohol was used.

Seven grams ethyl iodide, 15 grams isobutyl alcohol containing 15 per cent of water, and an excess of solid alkali gave over 100 cc. of gas burning like ethylene. In a second experiment, 10 grams ethyl iodide, 22.5 grams isobutyl alcohol (85 per cent), and 30 grams hydroxide gave 115 cc. gas, which burned as above and was absorbed by bromine with the exception of a few small bubbles. The yield in this experiment was only 8 per cent, but as it was an improvement over Lieben and Rossi's results with ethyl alcohol, we tried the same method with *n*-butyl iodide. Five grams of iodide, however, gave only 75 cc. of gas, so the experiments were carried no further. The slight solubility of potassium hydroxide in the alcohol used is perhaps responsible for the poor yield.

Absorption of the Butenes by Sulphuric Acid.

The apparatus described by Butlerow,[4] consisting of a glass tube 40–50 cm. long and 1.5 cm. wide, filled with glass beads, and surrounded by a jacket through which water can be passed, was used. The acid is allowed to drop in continually at the top and is drawn off at the bottom, the gas entering

[1] Compt. rend., **124**, 616 and 1358; **137**, 301.

[2] Ann. Chem. (Liebig), **158**, 166. See also Saytzew: J. prakt. Chem., N. F., **3**, 91.

[3] *Ibid.*, p. 166.

[4] Z. Chem., **13**, 238 (1870).

through a small tube at the base of the apparatus. The water in the jacket prevents any appreciable change in the temperature of the acid. The air was driven out at the beginning and the butene at the end of each experiment by carbon dioxide, which was absorbed by being passed through a bottle of alkali between the absorption apparatus and the collecting gasometer.

This method is not exact enough to give analyses of any great value, as the rate of absorption depends to a considerable extent on the rate of passage of the gas, and it was given up in favor of the Hempel pipettes. These experiments show, nevertheless, the difference in the additive power of the butenes and are of some interest.

The concentrations of sulphuric acid are given in parts of strong acid, of sp. gr. 1.8415 at 15° (97.7 per cent), to parts of water by weight.

	Parts H_2SO_4 to 1 part H_2O.	Temperature.		cc. gas		
		Acid.	Water.	Passed in.	Unab-sorbed.	Per cent absorbed.
Isobutene	1.5	..	..	..	..	None, or at most very little
"	2	0°	15–16°	450	50	90
"	2	17°	17°	150	..	100
"	2	10°	10°	50	..	100
Pseudobutene	2	15°	11°	85	75	12
54 cc. Isobutene 54 cc. Pseudobutene }	2	22°	13°	108	49–50[1]	...
Pseudobutene	3.75	18°	16°	32	20	37
"	3.75	18°	6°	50.4	32.2	36
n-Butene	3.75	17°	6°	55	37	33
Pseudobutene	4	16°	9°	43	8	81
n-Butene	4	17°	9°	55	28	49
Pseudobutene	5	20°	6°	66	5	91
n-Butene	3.5	18°	7°	41	41	none
"	3.5	18°	7°	20	20	none

In the above experiments the butenes were collected directly in the gasometers and, as it is impossible to prevent

[1] This series agrees well with the above experiments, which indicate that all of the iso- and a little of the pseudobutene should be absorbed. The dilution of the isobutene, however, probably prevents its complete absorption.

some air from getting in under such conditions, in the following experiments the gas was, in every case, liquefied by being passed through a U-tube with a bulb of about 2 cc. capacity at the bend, immersed in ice and salt. The sides of the tube were narrow so that when the bulb was full of liquid only a fraction of a cubic centimeter of air would be contained in the apparatus. The tube was removed from the freezing mixture and the gas collected in small glass gasometers over water that had been boiled. The mouths of the gasometers were kept constantly under water except when gas was being transferred to the burettes.

Hempel pipettes were used for these experiments,[1] and acids of a number of concentrations were employed. A mixture of 1.5 parts strong sulphuric acid to 1 part of water proved to be the best for comparison of iso- and pseudobutenes. The readings were made by transferring the gases to burettes.

Isobutene, 1.5 parts strong acid : 1 part water. Temp. 28°-29°.

A. Time. Minutes.	B. Reading cc.	C. Time interval. Minutes.	D. Decrease. cc.	E. Per cent absorbed.
0	68.2	0	0.0	0
10	21.2	10	47.0	69
20	7.6	10	13.6	89
40	1.9	20	5.9	97
160	1.6	120	0.3	98

The residue of 1.6 cc. burned with a yellow flame. In a second experiment, continued for eight hours, the residual gas would not burn, so that it is uncertain whether any other gas than isobutene was present. In any case it is impossible at present to state whether all of the slowing down in the rate of absorption is due to the presence of air or of some gas slowly absorbed.

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[1] They are not the best apparatus possible since the area of the surface of the liquid, and consequently the rate of absorption of the gas, varies with the volume of the latter present. For comparative experiments, however, approximately equal quantities of the gases were used.

Pseudobutene, 1.5 parts strong acid : 1 part water. Temp. 28°–29°.

A. Time. Minutes.	B. Reading cc.	C. Time interval. Minutes.	D. Decrease. cc.	E. Per cent absorbed.
0	63.4	0	0.0	0
10	62.7	10	0.7	1
20	62.4	10	0.3	2
40	62.2	20	0.2	2
150	60.5	110	1.7	5
175	58.4	25	2.1	8

Transferred to pipette containing
<div align="center">

5 parts strong acid : 1 part water.
</div>

177.5	12.8	2.5	45.6	80
182	6.7	4.5	6.1	90
194	4.6	12	2.1	93
300	3.4	106	1.2	95

Thus the pseudobutene is readily dissolved by strong sulphuric acid.

Mixture of 53.5 cc. Isobutene and 39.5 cc. Pseudobutene, 1.5 parts strong acid: 1 part water. Temp. 28°–29°.

A.	B.	C.	D.	E.
0	92.5	0	0.0	0
15	68.4	15	24.1	26
30	57.2	15	11.2	38
45	45.2	15	12.0	51
60	41.0	15	4.2	56
135	39.4	75	1.6	57
195	38.6	60	0.8	58

It is evident that when the rate of absorption has decreased to about that of the pseudobutene, the amount of gas remaining is nearly that of the above gas taken. The rate of absorption of isobutene is decreased about one-half by the presence of the other gases—approximately in proportion to the dilution. The following table, compared with the first one above, shows that the effect of change of temperature on the rate of absorption of isobutene is considerable, and other experiments might be given showing the same decrease.

Isobutene, 1.5 parts strong acid : 1 part water.   Temp. 21°–22°.

A. Time. Minutes.	B. Reading cc.	C. Time interval. Minutes.	D. Decrease. cc.	E. Per cent absorbed.
0	69.2	0	0.0	0
20	29.5	20	39.7	57
40	10.2	20	19.3	85
60	4.0	20	6.2	94
120	3.3	60	0.7	95
375	2.7	255	0.6	96

This residue, on transference to a pipette containing 5 : 1 acid, was hardly affected.   It will be noticed that only 39.7 cc. were absorbed in 10 minutes.   A second experiment with the mixture was made.

Mixture of 37.3 cc. Isobutene and 35.0 cc. Pseudobutene, 1.5 parts strong acid : 1 part water.   Temp. 21°–22°.

A.	B.	C.	D.	E.
0	72.3	0	0.0	0
20	57.2	20	15.1	21
60	42.2	40	15.0	42
100	36.6	40	5.6	49
120	35.8	20	0.8	50

The residue here is nearly equal to the amount of pseudobutene taken.

The difference in additive power of the normal and pseudobutenes is very much less than between these and isobutene, and is not great enough to permit of even an approximately quantitative separation.   The following tables show the relative ease of absorption of the two gases:

Pseudobutene, 3.5 parts strong acid : 1 part water.   Temp 29°–30°.

A.	B.	C.	D.	E.
0	43.7	0	0.0	0
20	35.8	20	7.9	18
40	29.4	20	6.4	33
60	24.3	20	5.1	44
80	19.5	20	4.8	55

n-Butene, 3.5 parts strong acid : 1 part water. Temp. 28°–29°.

A. Time. Minutes.	B. Reading cc.	C. Time interval. Minutes.	D. Decrease. cc.	E. Per cent. absorbed.
0	42.9	0	0.0	0
20	39.2	20	3.7	9
40	35.4	20	3.8	17
60	31.1	20	4.3	27
80	27.7	20	3.4	35

The pseudobutene is here absorbed almost twice as fast as the normal butene.[1]

Dehydration of Isobutyl Alcohol.

Various methods have been used for dehydrating isobutyl alcohol by means of sulphuric acid, with and without use of a catalyzer.

Erdmann[2] heats it with acid diluted with a small amount of water. In accordance with his directions 100 cc. alcohol, 44 cc. acid, and 16 cc. water were heated with a reverse condenser. About 4 liters of gas were obtained, 32 liters being the calculated quantity. Distillation of the residual liquid with steam gave 10–12 grams polymerized products boiling between 104° and 200°. In order to free the gaseous product from isobutene it was passed through aqueous hydrochloric acid which was kept saturated at —20° by a continuous current of gas. No tertiary butyl chloride was noticeable, but since it boils at 51° a small amount might have been formed and carried off. The amount of unabsorbed gas showed that, if present, isobutene could have been formed only in small amount. On passing the unabsorbed gas through bromine some was absorbed, and an oil boiling from 148° to 170° was obtained, which would indicate the presence of normal and pseudobutene in the original product.

[1] These experiments were carried out successively in the same pipette. In another series of experiments two pipettes with bulbs of somewhat different size were used. After a few measurements, the pipettes were changed and more readings taken. The diameter of the surface of the liquid in the two bulbs was measured roughly and a corresponding correction made in the figures for the absorption. The ratio was found to be in one case 1.8 : 1, in the other 1.6 : 1, the pseudobutene being absorbed faster. The true ratio is probably somewhere between these values and the value 2 : 1 found above.

[2] Erdmann-Bender: Chemische Präparate, II., 99.

Konowoloff[1] used 200 grams alcohol, 200 grams acid, 50 grams water, and 10 grams talc, which gave 30 liters gas, two-thirds of which, he states, was isobutene, as determined by the action of sulphuric acid diluted with an equal weight of water on the liquefied gases. In an experiment with 50 grams alcohol we obtained 6.66 liters gas, nearly the amount demanded by Konowoloff's statement. Distillation of the residual liquid with steam gave 17 grams of polymerized product, boiling at 104°–178°, with a higher boiling residue. In another experiment, with 100 grams of alcohol, 43 grams of this product were obtained.

Three hundred and fifty-six cc. of this gas were passed through two tubes of bromine cooled in ice, and, as only 24 cc. went through unabsorbed, 93 per cent of the product consisted of butenes. In a second experiment, with 250 cc. of gas, only 10 cc. went through, *i. e.*, 96 per cent was absorbed. The rate of absorption of this gas by sulphuric acid diluted with one-half its weight of water was measured, in a Hempel pipette and the mixture was thus found to contain about 60 per cent of isobutene. On treatment of the residue with acid diluted with one-fifth its weight of water, 18 per cent of the original amount remained unabsorbed after 24 hours. The original gas must, therefore, have contained, beside the butenes, a small amount of a saturated hydrocarbon, and also some of an unsaturated one which is not identical with any of the butenes.

According to Ipatiew,[1] when isobutyl alcohol is passed through a copper tube filled with zinc chloride and heated to about 500° a mixture containing all the butenes is formed, but when a copper or glass tube containing fragments of a graphite crucible or of aluminium oxide is used, only isobutene is obtained. This appeared to be the best method for preparing isobutene, but on repeating the experiments of Ipatiew we were not able to obtain the same results.

In our first experiment we used a Jena combustion tube,

[1] Ber. d. chem. Ges., **13,** 2395.
[2] *Ibid.*, **36,** 1990.

which was filled with pieces of a graphite crucible[1] that had previously been ignited in a covered Hessian crucible. The tube was heated in a L. Meyer[2] furnace for heating tubes; we found no difficulty in keeping the temperature of the tube fairly constant at 500°. Sixty-five grams of alcohol gave 29 liters of gas, but a large part of it was not isobutene. It could not be liquefied by passing through a tube cooled in ice and salt to —18°, nor was any alkyl chloride obtained by passing it through aqueous hydrochloric acid saturated at the same temperature, although isobutene unites readily with the acid under these conditions.[3] Five liters were then passed twice through bromine and only 1.75 liters were absorbed; in a second experiment with 6.5 liters, 2.5 liters were absorbed. The boiling point of the product thus obtained indicated the presence of more iso- than pseudobutylene bromide with, possibly, a little of the normal derivative. A second lot of gas was then prepared. Three liters were passed twice through hydrochloric acid at —18°, and nearly one liter was absorbed. Of the residue, 0.4 liter was absorbed by bromine, the oil formed boiling at 148°–164°—mostly near 155°, the boiling point of the pseudo compound. If only isobutene was absorbed by the hydrochloric acid, the ratio of iso- to pseudo-butene would thus be 2.3 : 1.

Aluminium oxide (Kahlbaum's C. P.) was then used as the catalytic agent. Eight and one-tenth liters of the gas were passed through bromine cooled in ice, and 4.5 liters were absorbed. A considerable amount of dibromide, boiling from 145° to 165°, was then prepared and fractionated. Only a partial separation was possible, but the results indicated that approximately two-thirds of the product was iso-, one-third pseudobutylene bromide, with a comparatively small amount which might have been the normal bromide. The residue unabsorbed in bromine burned with a slightly luminous flame, but not much carbon dioxide was produced by the combustion.

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[1] The crucible had been previously employed for another purpose, but the pieces used were as far as possible freed from foreign substance.

[2] Ber. d. chem. Ges., **16**, 1087.

[3] Le Bel: Bull. Soc. Chim., **28**, 460.

The temperature in the above experiment was measured by means of a mercury thermometer filled with carbon dioxide. After the last experiment the bulb was found to be enlarged, so that the temperature may have been considerably above 500°. A thermocouple was then used and the experiments repeated. With pieces of a new graphite crucible, 30 grams of alcohol gave 8 liters of gas in 50 minutes; with aluminium oxide the same amount of alcohol gave 6 liters in 65 minutes. The gases so obtained were analyzed by means of sulphuric acid in the Hempel pipettes.

Gas obtained with Graphite Crucible, 1.5 parts strong acid: 1 part water. Temp. 15°.

A. Time. Minutes.	B. Reading. cc.	C. Time interval. Minutes.	D. Decrease. cc.	E. Per cent absorbed.
0	100.5	0	0.0	0.0
40	73.6	40	26.9	26.9
70	59.3	30	14.3	41.2
120	48.2	50	11.1	52.3
150	46.2	30	2.0	54.3
210	44.6	60	1.6	55.9
405	42.3	195	2.3	58.2

Beginning with the sixth reading the isobutene may be considered as completely absorbed.

Same Gas as above, 5 parts strong acid : 1 part water.

A.	B.	C.	D.	E.
0	100	0	0.0	0.0
3	36.4	3	63.6	63.6
6	21.0	3	15.4	79.0
10	9.6	4	11.4	91.4
55	3.8	45	5.8	96.2
125	3.7	70	0.1	96.3

There thus appears to be about 55 per cent of isobutene, with about 2.5–3.0 per cent of gas not a butene at all. The latter result was confirmed by passing 0.90 liter of the gas through two tubes of bromine, when 20 cc. (2.2 per cent) were unabsorbed.

With the gas from aluminium oxide nearly the same results

were obtained, but the amount of isobutene was somewhat greater (65–70 per cent), and about 5 per cent was unabsorbed by 5 : 1 sulphuric acid. Some of the gas was passed through bromine cooled in ice and the unabsorbed gas analyzed by combustion. Thirteen and eight-tenths cc., mixed with 45.3 cc. of air, were exploded and underwent a contraction of 5.3 cc., no carbon dioxide being formed. If all had been hydrogen the contraction should have been 20.7 cc., while if there had been any hydrocarbon present some carbon dioxide should have been formed. It thus appears that there was approximately 1 per cent of hydrogen present in the original product, with about 3–4 per cent of air.

It appears from these experiments that slight differences in the catalytic agent may have considerable effect on the nature of the product obtained by the Ipatiew method and that the conditions necessary for the preparation of pure isobutene from isobutyl alcohol are not at present sufficiently well defined.

Preparation of the Higher Alkenes.

The amylene used was Kahlbaum's trimethylethylene, which is probably prepared[1] by dehydrating tertiary amyl alcohol with oxalic acid. The Kahlbaum product was boiled with sodium until the sodium remained unaltered, and then distilled through a column of beads. The whole product boiled at 37°–38°.

The only hexylene investigated was tetramethylethylene. This alkene was made by Couturier[2] from pinacone dibromide, and was considered pure until Kondakow[3] showed that it is a mixture. More recently Delacre[4] prepared a pure product, starting from dimethylisopropylcarbinol. This compound was prepared by the action of magnesium-methyl iodide on the ethyl ester of isobutyric acid. Delacre[5] found that the product obtained in this way was identical with that obtained from magnesium-isopropyl bromide and

[1] Z. angew. Chem., **93**, 202.
[2] Ann. chim. phys. [6], **26**, 461.
[3] J. prakt. Chem., N. F., **59**, 293.
[4] Centralb., **1906**, II., 498.
[5] *Ibid.*, p. 1719.

acetone, and that both gave bromides identical with that formed by addition of hydrobromic acid to tetramethylethylene. The yield of tertiary hexyl alcohol obtained from isobutyric ester was very poor. Twelve grams ester gave 7.5 grams product boiling at 117°–119°; and in another experiment 68 grams ester gave 21 grams product boiling at 118°–119°.5, or about 27 per cent of the calculated yield. The iodide was obtained by saturating with hydriodic acid gas and allowing the mixture to stand overnight, extracting with sodium carbonate, and then with water. After drying with phosphorus pentoxide and distilling in vacuum with beads, the product boiled constantly at 52° (23 mm.), and the yield was nearly quantitative. Tetramethylethylene was prepared from the iodide by means of alcoholic potash with excess of solid hydroxide in the proportions used with isobutyl iodide, the hydrocarbon being separated by addition of water to the mixture; also by treatment with 10 per cent aqueous potash, the amount used being the same as in the first case. The yield by the second method was somewhat better, but prolonged boiling, with frequent shaking of the mixture, was necessary to decompose all of the iodide. The tertiary carbinol formed and any ethyl alcohol present were removed by treatment with a small amount of phosphorus pentoxide. Fifty grams iodide gave 7.5 grams of product boiling at 71°–72°.5.

Diisobutylene was prepared according to Butlerow's[1] directions, by dissolving liquid isobutene in dilute sulphuric acid and heating to 100°. After 4–5 hours' heating there is little, if any, increase in the amount of polymerized product; indeed, the reaction is practically complete in a much shorter time. In one experiment sulphuric acid of sp. gr. 1.842 (= 97 per cent H_2SO_4) diluted with an equal volume of water was used. In this case nearly half of the product consisted of triisobutylene and high-boiling products, while, when the acid was diluted with an equal weight of water (Butlerow's proportions) about 80 per cent of the product was the dipolymerized derivative, which was easily purified. The total yield of polymerized product was 80–90 per cent

[1] Ann. Chem. (Liebig), **189**, 48 (1879).

of the isobutene used, 60 per cent of which distilled at 102°–102°.5 after being boiled with sodium, while a small amount of triisobutylene, boiling point 176°–178°, was obtained.

The hydrocarbons obtained from the mother liquors in the preparation of isobutene by the methods of Konowoloff and Erdmann[1] were dried and fractionated, but no sharp-boiling fractions could be obtained, even after repeated fractionation, the liquids distilling from 102° to over 260°.

Triisobutylene was prepared by passing isobutene slowly into sulphuric acid diluted with one-fifth its weight of water, and kept at about 4°, and allowing the mixture to stand overnight at room temperature. The oil which separated represented a yield of 60–70 per cent, but was not pure triisobutylene, as it boiled from 160° to higher than 200°. We varied the method by heating the solution to 100° as soon as the isobutene had all been passed in, also by using acid diluted with one-third its weight of water and working in the cold, but judging from boiling point the product was not improved in either case.

ADDITIVE POWER OF THE HYDROCARBONS.

Isobutene and Trimethylethylene.

Sulphuric Acid of Sp. Gr. 1.842 Diluted with One-half its Weight of Water.—Two tubes, each containing 2 cc. of acid, and one about 0.3 cc. liquefied isobutene, the other an equal volume of trimethylethylene, were cooled in ice water, then kept at this temperature and shaken. The butene dissolved in 4 minutes, the amylene in 12 minutes; after 1–2 hours the solutions became turbid, owing to the formation of polymerization products.

Sulphuric Acid with an Equal Weight of Water.—Four tubes, each with 2 cc. acid, one set of two with isobutene, the others with amylene, kept cold and shaken for 18–20 minutes. The butene had dissolved, but the volume of the amylene had only slightly decreased. The amylene tubes were then put in the shaker at room temperature. It required nearly two hours before solution was effected.

[1] See above.

Sulphuric Acid with Twice its Weight of Water.—A small amount of amylene stood more than 40 hours, part of the time in a shaking machine, before dissolving, while a larger amount of isobutene gave a clear solution in 12 hours with only occasional shaking.

Phosphoric acid was made up to 0.5 normal. Two tubes containing 1.5 cc. acid and 0.2 cc. amylene, and two others with the same amount of acid and as nearly as possible the same amount of isobutene, were shaken about 9 hours a day. After 55 days the butene was dissolved while the amylene was scarcely affected.

With *hydrochloric acid* (0.577 N) similar experiments were carried out with the result that the butene was dissolved in ten days, except a trace of yellow oil which did not disappear after 30 days longer and was probably polymerized product, while the amylene required 40 days.

It appears from these experiments that isobutene is dissolved by the acids used at least three times as fast as trimethylethylene.

Trimethylethylene and Tetramethylethylene.

Three Parts Sulphuric Acid with Two Parts Water.—Four tubes, each containing 0.360 gram acid, two with 0.030 gram of the amylene, and two with 0.036 gram of the hexene, the molecular proportion of hydrocarbon to acid being in each case 1:5, were kept in ice water, but shaken frequently. After 1.25 hours the amylene had dissolved (the solution on standing overnight began to polymerize), while the hexene was not noticeably changed.

Sulphuric Acid with One-half its Weight of Water.—Tubes with acid and hydrocarbon in the same molecular proportion as above. The amylene dissolved in 35 minutes, while the hexene did not change in 6 hours, although on standing overnight nearly all of it went into solution. Polymerization takes place faster in the amylene than in the hexene solutions, having already begun with the former after 24 hours in the above experiment. After a week, however, a layer of oil of nearly the same thickness as the original one

had appeared in the hexene tubes. After 15 days these were opened, the oil was dried with a little phosphorus pentoxide, and distilled. The boiling point was considerably above 100°, which is sufficient to show that polymerization had occurred.

With *sulphuric acid diluted with one-fourth its weight of water*, the tubes lying on their sides in ice water, the hexene was found to dissolve in 20 minutes and to begin to polymerize in 2.5 hours.

With *hydrobromic acid*, similar results were obtained. An aqueous solution of 4.56 N acid dissolved the amylene in 4 hours but showed no noticeable action on the hexene in 56 days. With 2 N acid the amylene dissolved in 0.75 hour but the hexene little, if at all, in 50 days. It was also found, both by titration of the acid and by the boiling point of the oily layer, that the hexene had not formed any hexyl bromide.

The difference between the tri- and the tetramethylethylene is thus much greater than between the first compound and isobutene. In the former case the ratio is at least 12 : 1, when 2 : 1 sulphuric acid is used.

Tetramethylethylene and Diisobutylene.

The hexene having been found to dissolve in 4 : 1 sulphuric acid in a few minutes, diisobutylene was tried with the same acid. This did not dissolve at all, judging from the thickness of the oily layer, but after 12 days' standing, most of the oil was found to boil above 140°, although some of the original substance (boiling point 102°–103°) was still present.

With *8.06 N hydrobromic acid* four tubes were prepared and shaken about 9 hours a day. Two containing the hexene were opened after 50 days, two with the octene after 65 days. In the former, 80 per cent of the hydrocarbon had formed bromide, while the presence of a tertiary carbinol was ascertained by diluting the solution, distilling, and salting out the distillate. The boiling point of the oil in the tubes —120°–140°—indicated that none of the original hydrocarbon (boiling point 72°) was left. In the octene tubes 32 per cent of the hydrocarbons had been converted into bromide. The

oil distilled mostly at 102°–105°, although there was a little of the higher boiling products. This result shows that considerable diisobutylene (boiling point 102°–103°) was still unchanged.

AN ELECTRICALLY-CONTROLLED GAS REGULATOR.

By E. Emmet Reid.

In some work which is being carried on at various fixed temperatures and where accurate and reliable gas regulation is required, the following regulator has proved entirely satisfactory.

A glass U-tube of about 8 mm. internal diameter (T T T, Fig. 1) is provided with a side tube V and is enlarged at the top for the reception of a small rubber stopper, S S. Through this stopper passes a tube, N O, with an external diameter 1 mm. less than the internal diameter of the U-tube. The U-tube is filled with mercury, H H H, to the level L L, a millimeter or so below the end of the tube N. The weight W is a piece of iron about 7 mm. in diameter and 15 to 20 mm. long. This is suspended freely from a hook, C, on the armature of an electro-magnet, M M. The armature is held up by a spring which is fastened rigidly to the block B. The spring is adjusted to support the weight but to yield quickly to the magnet. The length of the wire C must be such that its end will have a vertical motion of 1 or 2 mm. Greater motion than this is not required but will do no harm. The iron rod W must be suspended flexibly and freely rather than rigidly so that it acts simply by its own weight on the mercury. If the sudden motion of the armature be rigidly and suddenly transmitted to the mercury, the latter may splash into the side tube V.

The gas enters at N and, normally, flows under the lower end of this tube up through the annular space E and out to the burner through the side tube V. When the electromagnet is actuated the lowering of the weight W causes a corresponding elevation of the mercury at O and cuts off the gas. A pin hole at P allows enough gas to pass through to

keep the burner lit. In constructing the apparatus two or three very small pin holes may be made and closed with paraffine. One or more of these, as the size of the burner or stove may require, can be opened with a hot needle to allow the
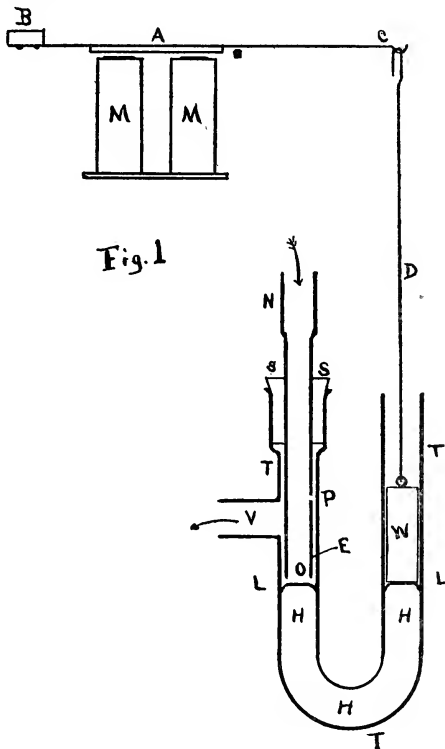
Fig. 1

passage of gas for a pilot flame, or the burner may be provided with an independent supply of gas to keep it lit. The surface tension of mercury is so great that though the weight W fits only loosely in the tube the mercury will not enter the annular

space around it. Thus W acts as well as an air-tight piston. On the other side the pressure of the gas is not sufficient to drive the mercury into the annular space there. To get the full advantage of this fact the gas should be made to enter through the central tube N and go out at V, and not the reverse.

As a motion of only 1 or 2 mm. is required for the weight W, and as this weighs only about 7 grams, the work required of the electro-magnet is very slight.

For the electro-magnet an ordinary electric bell of the cheapest form may be used, the vibratory make-and-break being short-circuited and the bell removed. The connection D may then be hung on the end of the clapper. The magnet may be wound up to 20 ohms to economize current. With this resistance in the electro-magnet, a single storage cell will give excellent service, while with less resistance, an ordinary dry cell is all that is required.

Instead of being suspended, W may be floated on the mercury, the amount of which is so adjusted that the gas can pass properly. In this case, instead of using the electro-magnet, a coil of wire of suitable size and length is wound around the limb of the U-tube containing W. The resistance of the coil should be from 5 to 20 ohms, according to the battery used. This coil is placed somewhat below the center of W. When the current is passed through this solenoid, W is drawn down and the gas cut off as before. W should be made of the softest iron obtainable. This plan requires more current but is simpler.

The apparatus can be controlled by any of the forms of electrical regulators on the market, in which a contact is made when a certain temperature is exceeded and broken when the temperature goes down. As these regulators may be made of extreme sensitiveness the regulation of temperature to any required degree of accuracy may be accomplished.

The advantage of this form of regulator is that it can be made quickly and easily out of materials at hand in the chemical laboratory. It may be readily cleaned. The large gas opening permits of much fouling of the mercury before cleaning is required.

In Fig. 2 is shown another regulator based on the same principle. It is made of a block of cast iron, about 2 x 2 x ¾ inches or 60 x 60 x 18 mm., into which holes are drilled. As most of these correspond to the tubes in the other figure and are lettered in the same way they will not be redescribed. The main holes may be of the same size as the tubes in Fig. 1,

Fig. 2
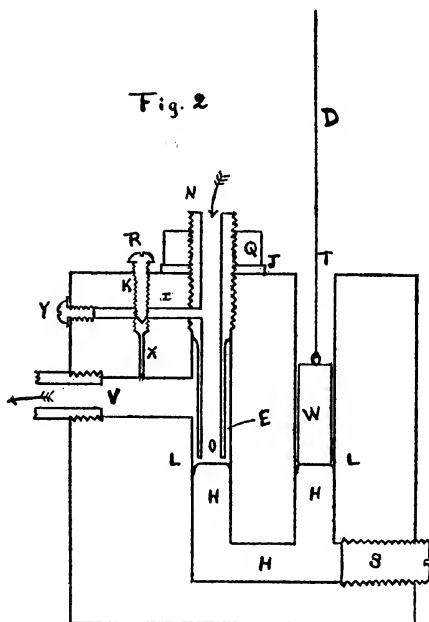
or may be of any size suitable for the supply of gas required. S is a plug which may be used to regulate the height of the mercury in the U-tube. Should the mercury become foul it may be removed by taking out S, cleaned, and replaced. The inlet tube N O is made in the shape shown, its lower part being turned down on the lathe so as to leave the proper space

for the gas. Its upper portion is threaded with straight thread so as to screw into the block. When it is put in place the lock-nut Q is screwed on firmly over the lead washer J. Then the hole I is drilled through the block and into the tube N. The outer end of this hole is closed by the screw plug Y which is provided with a lead washer. The hole K is drilled so as to intersect I, and is continued by the small hole X which opens into the outlet V. A pointed screw, R, serves as a needle valve to regulate the by-pass and supply any amount of gas desired to keep the burner or stove lit.

A gas-pipe thread may be cut on the extreme upper end of N and the supply pipe screwed on directly. The hole V is tapped to receive the iron gas pipe for the burner. The advantage of this form over the other is that, being entirely of metal, it is unbreakable and compact, and eliminates any danger of fire. The operation is the same as that of the other form.

The work of which this is a part is being carried on by the aid of a grant to Prof. S. F. Acree, by the Carnegie Institution.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
January 5, 1909.

AN APPARATUS FOR THE PURIFICATION OF MERCURY.

BY L. JUNIUS DESHA.

The purification of mercury has often been accomplished in the laboratory by pouring the metal from a funnel with a minute capillary outlet through a column of dilute nitric acid (or other cleansing solution) about one and one-half meters in height. When repeated sufficiently often, this process is very effective. But the frequent attention necessary for returning the mercury from the lower receiver to the funnel seriously interferes with other work during the long time required for satisfactory purification, and there is therefore always a natural tendency to stop the operation too soon. Having to purify a considerable quantity of mercury *very thoroughly* I cast about for some means of avoiding this waste

of time. Professor S. F. Acree suggested to me the automatic principle of the apparatus now to be described and I am further indebted to him for assistance in working out some of the details.

A and B (Fig. 1) are tubes 22 mm. in diameter and 90 and 35 cm., respectively, in length, connected by fusion of their lower ends to the small curved tube which bears the glass

Fig 1
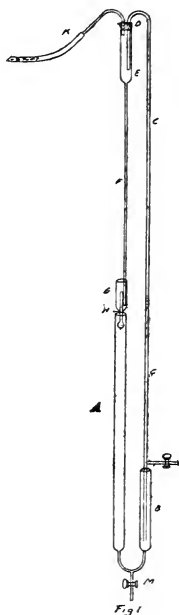
stop-cock M. C is made of thick-walled glass tubing 1.5 mm. in bore and about 200 cm. in length, to which a side tube with glass stop-cock, L, is fused just above B. Its lower end hangs loosely in B near the constriction and the upper end passes through the rubber stopper D into the tube E. The latter is 20 mm. wide and 150 mm. long, terminating in the

thick-walled capillary F (76 cm. long) which extends to the bottom of the mercury trap G. The capillary tube H is fused into G; its upper end is expanded and extends 25 mm. above the outlet of F while its lower end, extending 10 cm. into the liquid in A, is blown into a small bulb containing several very small holes. A second tube leads from E through D to the suction pump.

Mercury is poured into A or B in any desired quantity (provided only that it extends above the lower end of C) and then the remainder of A is filled with the purifying agent, which is usually one per cent nitric acid. The trap G having been filled with mercury to the level of the top of H, the suction pump is turned on. Under the diminished pressure thus produced in C and E, mercury is drawn from B into C, the stop-cock L being so adjusted that alternate small portions of mercury and air are drawn up into E.[1] At the same time mercury is, of course, drawn into F from G until a pressure is attained which balances that in C. The mercury drawn through C into E runs down through F into G, then over the top of, and into, H and is discharged into the cleansing solution in A through the minute openings in the bulb of H.

Such an apparatus has been in use here now for several weeks and the results have been most satisfactory. The advantages which it offers may be summarized as follows. The process is perfectly continuous for a given lot of mercury and requires absolutely no attention after once being started. The apparatus may be used equally well for large or small quantities of mercury. By suitable and easy adjustment of the stop-cock L, the maximum efficiency for any given pump may be readily attained. The cleansing solution, when exhausted, may be siphoned off and replaced by a fresh one; pure mercury may be withdrawn at M. As the apparatus consists only of glass (with the exception of the rubber stopper D which does not come into contact with the mercury) there is no chance for the introduction of impurities, and the individual parts may readily be removed and cleaned when

[1] Dr. B. B. Turner has called my attention to a similar arrangement used by Boltwood in his modification of the Sprengel pump. Cf. THIS JOURNAL, **19**, 76.

necessary. When a No. 3 Chapman pump is attached to the apparatus 100 cc. of mercury are passed through the cleansing solution once in about eight minutes.

Though the very fine division of the mercury, as it passes through the nitric acid, insures large surface and therefore very thorough cleansing, I propose to still further increase the purity of the product by combining an electrolysis with the present arrangement. This can be accomplished very simply. A platinum plate will be hung in A beside the bulb of H and surrounded by a silk bag. A small platinum wire will make electrical connection with the mercury in H which will be made the anode. A small current will then be passed between it and the platinum plate in the nitric acid. The impurities in the minute charged globules leaving H should electrolyze out very easily, while the bag will prevent any deposit formed on the cathode from dropping to the main body of mercury below.

THE JOHNS HOPKINS UNIVERSITY,
December 24, 1908.

REPORTS.

HYDROGEN PERSULPHIDES.[1]

Persulphides of hydrogen were discovered by Scheele in 1777; since then many prominent chemists have studied these substances and have devised new methods for their preparation. We find references in text-books to compounds of the compositions H_2S_2, H_2S_3, H_2S_4, H_2S_5, but no one has hitherto succeeded in obtaining any one of these substances in pure condition.

As raw material Bloch used crude sodium polysulphide, which he made by heating crystallized sodium sulphide ($Na_2S + 9H_2O$) with a weighed amount of sulphur on the water bath; the sodium sulphide melts in its water of crystallization, dissolving the sulphur. The product, which is dissolved in water, approaches the compositions Na_2S_2, Na_2S_3, Na_2S_4, or Na_2S_5 according to the proportion of sulphur used. The solution is put in a dropping funnel under hydrogen pressure and is run slowly into a large beaker containing hydro-

[1] Abstract of four articles by Ignaz Bloch and pupils in Ber. d. chem. Ges., **41,** 1961 (1908).

chloric acid and ice, which is kept at a temperature of $-10°$
by means of a freezing mixture. The contents of the beaker
are constantly stirred. An emulsion is thus obtained which
deposits a yellow oil. This oil is dried by calcium chloride
which has been previously treated with dry hydrochloric
acid gas. Otherwise the calcium chloride is alkaline enough
to partly decompose the hydrogen persulphide. All vessels
which come into contact with these persulphides must like-
wise be treated with hydrochloric acid gas to neutralize the
alkalinity of the glass. Indeed, Bloch ascribes the failure of
previous workers, from Scheele down, to obtain pure sub-
stances to the neglect of this precaution.

By distilling 50 cc. crude polysulphide at a pressure of
only 2 mm., 8 cc. distillate in three fractions were obtained.
The middle fraction proved to be pure hydrogen trisulphide,
H_2S_3.

Hydrogen trisulphide is at ordinary temperatures a pale
yellow liquid; at low temperatures it is colorless. It has the
consistency of olive oil and a specific gravity of 1.496 at 15°;
it boils under 2 mm. pressure at 69°, and solidifies at $-52°$ to
$-59°$. Its odor is penetrating and disagreeable, recalling
that of sulphur chloride and camphor, and its vapors attack
the mucous membranes. It decomposes gradually on stand-
ing, more quickly in the light than in the dark, forming hy-
drogen sulphide and free sulphur. It is decomposed by alka-
lies and by alcohol. It is soluble in ether, benzene, and car-
bon disulphide, forming comparatively stable solutions. It
dissolves sulphur at ordinary temperatures, but on the addi-
tion of benzene the dissolved sulphur is precipitated.

In the preparation of hydrogen trisulphide Bloch protected
the mercury pump by means of a potash bulb between the
pump and the receiver. Noticing that the potash turned
yellow, he introduced a second receiver and found that while
the trisulphide condensed in the first receiver as before, a
more volatile liquid collected in the second. This proved to
be hydrogen disulphide, H_2S_2. He also made the disul-
phide by distilling pure trisulphide at 100° under 20 mm.
pressure. About one-third of the trisulphide changed to
disulphide, one-third distilled undecomposed, and the remain-
der was decomposed into hydrogen sulphide and sulphur.

Hydrogen disulphide, H_2S_2, is a clear yellowish liquid at
ordinary temperatures. Its specific gravity is 1.376. It
is more stable than the trisulphide, as it can be distilled in great
part without decomposition under atmospheric pressure at
74°–75°. It does not solidify in a mixture of ether and solid

carbon dioxide, differing in this respect from the trisulphide. In all other respects it resembles the trisulphide but is chemically more active.

The analytical data for both of these sulphides show that the substances obtained were pure. The methods used were: (a) determination of the amount of hydrogen sulphide liberated by the action of acid; (b) determination of hydrogen, by combustion with lead chromate; (c) determination of the total sulphur by the method of Carius. In making the sulphur analyses Bloch found that the fumes of the nitric acid, acting on the trisulphide, caused an explosion during the sealing of the tube; to prevent this he froze the nitric acid in the tube, and then added the weighed sulphide in a glass-stoppered weighing bottle, sealed the tube, and allowed the acid to thaw in a tube furnace.

With an ordinary vacuum distilling apparatus the yield of pure sulphides was variable and unsatisfactory. Bloch therefore devised an apparatus so ingenious and useful for fractional distillation that it seems well to copy his description of it and of the method of work.

The 300 cc. Anschütz flask A (Fig. I.) is connected by a long condenser with the receiver B (a 150 cc. distilling bulb), and this, in turn, with the vessel C which is cooled by a mixture of ice and salt. The flask A is also connected by the tube E to the deep U-tube F. The T-tube H leads through soda-
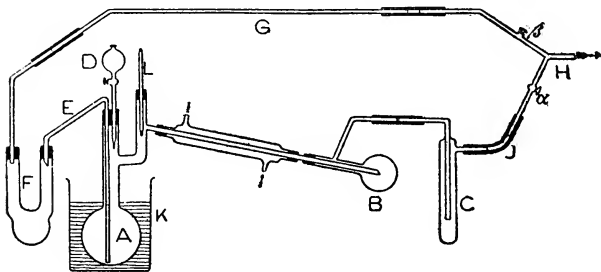
Fig. I.

lime and calcium chloride tubes and a manometer to a mercury pump. By opening or closing alternately the stopcocks α and β, the pump is connected either with the vessel C or through the tube G with the U-tube F. The flask A is filled through the dropping funnel D.

The method of procedure is as follows: After hydrochloric acid gas has been passed for 10 minutes through the whole apparatus, the glycerol bath K is heated to 110°–125°. The stopcock α is then opened and β is closed and the pressure is reduced to about 20 mm. About 15 cc. of crude hydrogen polysulphide are allowed to run slowly into the flask; in 30 seconds the liquid foams and distils evenly into the receiver B, the temperature of the vapors rising above 60°, as shown by the thermometer L. The foaming and distillation soon nearly cease almost entirely. Stopcock α is now closed and β opened, the residues in A being drawn over into F. The stopcocks are then reversed and a new distillation with another 15 cc. portion of polysulphide begun.

The distillate in A is nearly pure hydrogen trisulphide; by drawing a little air over it, traces of hydrogen sulphide and some trisulphide are removed, and by freezing it and pressing the frozen mass it is completely purified. The distillate in C is hydrogen disulphide and is purified for analysis by a single distillation at atmospheric pressure. The yield from 100 cc. crude polysulphide is from 30 to 33 cc. of trisulphide and from 10 to 15 cc. of disulphide.

The apparatus described will be found convenient for distilling any substance which cannot be distilled in larger portions without general decomposition.

Bloch proposes several constitutional formulas for the di- and trisulphides, but admits that he has not thus far enough experimental evidence to confirm any one of them.

He does not believe that hydrogen trisulphide is the last member of the series H_2S_n. As the strychnine salt of the hexasulphide, H_2S_6, has been carefully studied by A. W. Hofmann, and its brucine salt by E. Schmidt and later by Bruni and Borgo, who also made the benzyldiamine salt, while the brucine salt of the octosulphide, H_2S_8, has been made by Döbner, Bloch thinks there can be no doubt as to the existence of the hexa- and octosulphides of hydrogen.

As the disulphide, H_2S_2, is formed by heating the trisulphide H_2S_3, Bloch does not believe that the former is present in the crude polysulphide, nor does he believe that this crude polysulphide made from crude Na_2S_4–Na_2S_5 contains the trisulphide, for the following reasons: pure trisulphide dissolves in benzene in any proportion without decomposition. Sulphur dissolves freely in the trisulphide, but if benzene is added to this solution the dissolved sulphur is precipitated. If then crude hydrogen polysulphide were simply a solution of sulphur in hydrogen trisulphide, benzene should precipitate the

dissolved sulphur. As a matter of fact, the polysulphide dissolves freely in benzene, forming clear solutions. This leads Bloch to the conclusion that all of the sulphur in the crude polysulphide is chemically combined with hydrogen, that the trisulphide is formed by a breaking down of higher polysulphides contained in the crude material, and that probably some or all of these higher members of the series H_2S_n can be isolated in pure condition.   E. R.

PREPARATION OF ARGON FROM AIR BY MEANS OF CALCIUM CARBIDE.

Franz Fischer and Oskar Ringe[1] have worked out a method whereby they are able to obtain argon of a high degree of purity in comparatively large quantities with simple and inexpensive apparatus.

Atmospheric air contains 0.937 per cent, by volume, of a mixture of the so-called "noble gases," which, in turn, consists of 99.75 per cent of argon and 0.25 per cent of helium, neon, krypton, and xenon. Cavendish first noticed that when air is sparked in the presence of an excess of oxygen and the oxides of nitrogen and the remaining oxygen are absorbed, about 1/120 of the original volume of air remains unabsorbed. Ramsay and Rayleigh later used this method to isolate argon; in this manner the latter was able to obtain 2 liters of this gas. Afterwards these same investigators employed magnesium to absorb the nitrogen after the oxygen had been removed by means of copper heated to redness. Maquenne suggested the use of a mixture of lime and magnesium, which react according to the equation

$$CaO + Mg = MgO + Ca,$$
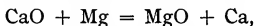
the calcium then energetically absorbing the nitrogen with the formation of calcium nitride, Ca_3N_2. As calcium can now be prepared electrolytically at quite a low cost, this metal has, of late years, been used almost exclusively to absorb the nitrogen.

Fischer and Ringe have found that at 800° a mixture of 90 per cent of finely pulverized calcium carbide and 10 per cent of anhydrous calcium chloride absorbs the nitrogen in air quantitatively, forming calcium cyanamide and carbon according to the equation

$$CaC_2 + N_2 = NC.NCa + C.$$
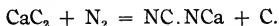
As the price of the carbide is low, it is used to absorb the oxygen also. The final products in this case are lime and free

[1] Ber. d. chem. Ges.; **41,** 2017 (1908).

carbon, carbon dioxide and monoxide being formed as intermediate products. The carbide thus serves to absorb everything but the noble gases and hydrogen which may be formed from traces of water present in the calcium chloride.

The absorption vessel consists of an iron box with walls 8 mm. thick, 50 cm. long, and 17 cm. wide and provided with inlet and outlet tubes of the same material and suitably cooled at the points where they emerge from the box. It is placed in a brick furnace and heated with gas burners. A vessel of these dimensions will hold 7 kilograms of carbide. After it has been exhausted and heated to remove the gases and tarry products formed by the action on the carbide of the water which is always present in the calcium chloride, it is connected with a series of tubes and gasometers arranged in the order shown below:

$$P_2O_5 \twoheadleftarrow H_2SO_4 \twoheadleftarrow KOH \twoheadleftarrow \text{heated } CuO \twoheadleftarrow CaC_2 \twoheadleftarrow \text{dry air}$$

circulating pump $\rightarrow$ gasometer————————⌐

reserve gasometer
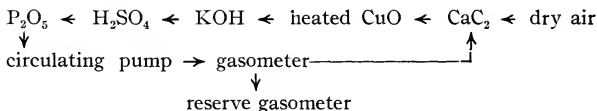
Dry air is now slowly admitted until the pressure in the whole apparatus is about equal to that of the atmosphere. The supply of air is then shut off, and by means of a simple mercury circulating pump, which is fully described in the authors' paper, the gases in the apparatus are drawn repeatedly over the heated copper oxide and the series of absorbents into the gasometer, and back again into the carbide vessel, etc., until there is no further diminution in pressure. Any hydrogen which may be formed or carbon monoxide which is not acted upon by the carbide is burned by the copper oxide to water and carbon dioxide, respectively, and is absorbed in the next tubes in the series. The argon is finally drawn into the reserve gasometer, a fresh supply of air admitted to the apparatus, and the process repeated until the carbide is exhausted. In this way, with 7 kilograms of the carbide mixture the authors obtained in 22½ hours 11 liters of "Rohargon," *i. e.*, a mixture of 99.75 per cent argon and 0.25 per cent of the other noble gases. Specific gravity determinations showed that there could not be more than 0.1 per cent of nitrogen in the product. C. A. R.

REVIEWS.

A Treatise on Qualitative Analysis and Practical Chemistry. Adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc., Lond., Emeritus Professor of Chemistry in the University College, Nottingham. Eighth Edition. London: J. and A. Churchill; Philadelphia: P. Blakiston's Son and Co. 1908. pp. xxiii + 518. Price, $3.00.

This volume is unlike any other of our text-books. Much of the matter is copied from the "Elementary Practical Chemistry" by Clowes and Coleman (reviewed in This Journal[1]), but although the field is restricted to qualitative analysis, the size and scope of the book are much enlarged.

A large part of it is given to the preparation and properties of gases, and the properties of substances, both organic and inorganic. Much space is devoted to apparatus, laboratory fittings, and other matters interesting to the teacher more than to the student.

The methods are all the common well-tried ones, and do not go beyond the ordinary needs of the technical chemist. No use is made of any phase of physical chemistry.

The book can be recommended as a good manual for teachers in high schools and technical schools, and for technical chemists.

E. R.

Laboratory Manual of Qualitative Analysis. By Wilhelm Segerblom, A.B., Instructor in Chemistry at the Phillips Exeter Academy. New York, London, Bombay, and Calcutta: Longmans, Green, and Co. 1908. pp. xii + 136. Price, $1.25.

This is a good laboratory manual for beginners, clearly written and full of detail. It contains nothing original or novel.

E. R.

Elektroanalytische Schnellmethoden. Elektroanalyse unter Bewegung von Elektrolyt oder Elektrode. Von Dr. Ing. A. Fischer, Technische Hochschule, Aachen. Mit 41 Abbildungen und 136 Tabellen. Stuttgart: Verlag von Ferdinand Enke. Preis, M. 9.40.

This book of 300 pages comprises volumes IV.-V. of "Die Chemische Analyse" by Dr. B. M. Margosches. The excellent presentation of the theory of electroanalysis, as set forth in the first 70 pages of this work, fills an important gap in the literature of analytical chemistry. Many chemists have avoided the use of electroanalysis, or have not obtained good results from these methods, because of a lack of understanding of the subject. To obtain even a working knowledge from the original literature required the expenditure of

[1] 38, 251; 39, 311.

a great deal of time and patience. To chemists thus situated, and to the student of the subject in general, the book will prove of great value.

The theory of the reduction and separation of metals and the bearing of polarization on the subject is ably handled from the standpoint of the well-known Nernst formula. Considerable space is devoted to the important rôle played by diffusion and complex salts, and to the influence of temperature and of stirring. More might have been profitably said, perhaps, with regard to the various factors governing the form of metallic deposits, and exception might be taken to some of the statements under this head on pages 41–42. No mention is made of Bancroft's comprehensive articles on this subject.[1] Some thirty pages, which are illustrated by numerous very excellent drawings and photographs, are devoted to the description of modern apparatus and to the sources of current.

In the practical part of the book the elements to be considered are divided according to their electrical behavior into six groups. A great deal of information about the various procedures for determining the individual metals is condensed into tabular form, and pains have been taken with the numerous references to the original literature. The author does not give his "besondere Gründe" for leaving out the work done with the mercury electrode, but the advisability of making such an omission is open to question.

In the last part of the book a number of practical determinations, such as the rapid analysis of brass and bronze, are given. Most of these have been carried out in the author's own laboratory. To any one interested in electroanalysis this book is highly recommended.   E. B. SPEAR.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By DR. H. MEYER, Professor at the Imperial and Royal German University, Prague, and J. BISHOP TINGLE, PH.D., F.C.S., Professor of Chemistry at McMaster University, Toronto, Canada. Third Edition, Revised. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1908. pp. XIV + 218. *see errata p. 57*

The new matter in the second edition of this excellent treatise on the qualitative and quantitative determination of radicles in carbon compounds is found in the appendix of 55 pages. Recent uses of alkylating agents, isocyanates, the Zeisel method, etc., are described in detail. One of the most important features of this book is the large number of references, a feature which English texts on chemistry too often lack.
                                                                S. F. ACREE.

[1] J. Phys. Chem., **9**, 277; **12**, 36.

AMERICAN

CHEMICAL JOURNAL

THE ABSORPTION SPECTRA OF SOLUTIONS OF A
NUMBER OF SALTS IN WATER, IN CERTAIN NON-
AQUEOUS SOLVENTS, AND IN MIXTURES OF
THESE SOLVENTS WITH WATER.

By Harry C. Jones and John A. Anderson.

[TWENTY-FOURTH COMMUNICATION.]

(The following paper records some of the results obtained
in an investigation on the absorption spectra of solutions
carried out under a grant from the Carnegie Institution of
Washington. The work as a whole is now being published
by the Institution,[1] and much of this paper is taken directly
from that publication.)

INTRODUCTORY.

The work on the absorption spectra of solutions, of which
this forms a part, was begun in the fall of 1905 and continued
during the year 1905–6 by Jones and Uhler. The results
obtained are given and discussed in Publication No. 60 of the
Carnegie Institution of Washington, entitled "Hydrates in
Aqueous Solution," by H. C. Jones.[2] The first part of that

¹ Carnegie Institution Publication, No. 110 (1909).
² Cf. This Journal, **37,** 126, 207 (1907).

work dealt with the effect of adding various dehydrating agents to solutions of colored salts; the second part, with the change in the absorption spectra produced by adding water to nonaqueous solutions. In the latter phase of the work, however, the concentration of the colored salt was varied in the solutions used in making any one spectrogram; but as the change in the spectrum observed was always the same qualitatively as would be expected from the change in concentration, it was deemed advisable to carry out again this part of the earlier work, keeping the concentration of the colored salt constant.

The salts used in the previous investigation were: Cobalt chloride, copper chloride, and copper bromide. In this investigation cobalt bromide was added to the above list of compounds. The spectrograms we have obtained show the same general change in the absorption as was observed in the earlier work, thus proving that it was not due to change in concentration, but to some action of the water added.

If we assume that the absorption of light is due to vibrating, charged particles, or electrons, which are associated with ions, molecules, or groups of one or both of these, it is natural to expect that the character of the absorption will, in general, depend upon the nature of the system with which the vibrating, charged particle is associated. In what follows, the system made up of the charged particle and whatever it is associated with will be spoken of simply as the "absorber."

The simplest case of an absorbing solution would be one containing only one kind of "absorber," and we shall speak of it as a "simple" absorbing solution. Such a solution does not in all probability exist, but is perhaps closely approached in such cases as the very dilute solutions of the salts of permanganic acid studied by Ostwald and others. Such a solution the absorption of light of a given wave length would be simply proportional to the number of absorbers in the path of the light (Beer's law); and if the absorbers are not changed by adding more of the solvent it follows at once that if the product of concentration and thickness of layer of the solution is kept constant, the absorption will be unchanged. Also, if we have a solution containing several kinds of absorbers,

each acting independently of the others, the same statement would be true; in other words, the absorption spectrum of a mixture of simple solutions will be the sum of the absorption spectra of the constituents.

If the concentration is very great, the absorbers may be so close together that they cease to act independently of each other; in such a case, even if the solution is a simple absorbing one, Beer's law *may* cease to hold. In general, however, we may say that for simple absorbing solutions or mixtures of these, Beer's law will hold.

Actual solutions always differ more or less from the ideal simple solutions on account of the changes produced by dilution. These changes are due to *association, dissociation,* and *solvation.*

The molecules of the dissolved substance may combine with each other, forming more or less complex aggregates, each of which will, in general, have its own peculiar power of absorbing light. The composition of the aggregates will depend upon temperature and concentration, and hence, if a solution containing such aggregates is diluted, we should expect to find deviations from Beer's law even if the temperature is kept constant.

The molecules of a great number of substances, when dissolved, dissociate into two or more ions, the amount of dissociation depending upon the concentration. It is to be expected that the absorption of the ions into which a molecule dissociates will be different from that of the molecule itself; and, consequently, on diluting an electrolyte we should expect to find deviations from Beer's law, unless the solution is so dilute that it may be considered as completely dissociated.

We may also have various combinations of molecules, aggregates of molecules or ions, not only with each other, but also with the molecules of the solvent, the nature of which will depend both on temperature and concentration, and each of which may have a different power of absorbing light. If a simple, colored electrolyte like cobalt chloride, for example, is dissolved in water, we see at once what a complicated system the solution is; and it is not surprising that, in spite of the

great amount of work which has already been done on this one salt alone, we are still far from being able to give a satisfactory account of its absorption spectrum.

A satisfactory account of the absorption of any salt in solution requires a knowledge of the kinds of absorbers the salt forms, and of the amount of each for any given set of conditions. Given this knowledge, it would be necessary to determine what would be the absorption spectrum if the solution contained only one kind of absorber. This could be done as follows: Suppose a salt in solution gives rise to the absorbers A, B, C, D, E, etc., the amount of each of which is supposed to be known under all conditions of temperature, pressure, concentration, etc. Vary the conditions in such a way that all the absorbers except A, for example, are kept constant, and note the change in the spectrum; this change is due to A alone, since by hypothesis no other absorber is varied. Repeat, keeping all except B constant, and so on. By this process of elimination we should eventually arrive at a complete knowledge of the absorption due to each absorber, and could hence predict exactly what would be the absorption of any solution whatever of the salt in question. Unfortunately our knowledge of the parts formed when a salt is dissolved is still very vague.

We have methods for measuring dissociation, so we may regard the number of ions and the number of undissociated molecules as known for different conditions. Regarding aggregates and solvates, however, our knowledge is very general, indeed. Determinations of molecular weight give some idea concerning the existence or nonexistence of aggregates, and the methods of Jones and others furnish similar ideas about solvates; but the knowledge gained thus far is not definite enough to enable us to perform experiments along the lines indicated above. A great deal can, however, be learned not only about absorption, but also about the nature of solutions, by the study of absorption spectra under conditions which are varied as much as possible.

The methods commonly employed are:

(1) To keep the concentration constant, varying the depth of the cell and photographing the spectra of successive depths

one beneath the other, so that the complete spectrogram gives an idea of the intensity of absorption for the different regions of the spectrum, besides locating the absorption bands.

(2) To keep the depth of cell constant and vary the concentration. The results here should be identical with those obtained by keeping concentration constant and varying the depth of cell, provided the solution is of such a nature that Beer's law holds; in general, however, the two methods give quite different results, owing to the change in the nature of the absorbers produced by dilution.

Another method is that followed in the present work, namely, to vary both depth of layer and concentration in such a manner that the product of the two remains constant. If the nature of the absorbers is not changed by dilution, this method leaves the number of absorbers in the path of the beam of light constant, and hence the spectrum for successive solutions should be identical; or, what amounts to the same thing, the width of the absorption bands, as shown by the spectrogram, should remain constant throughout. Any deviation from Beer's law would at once be seen in a change in width or position of the bands as the concentration is varied.

A variation of this method also employed in the present work is to vary the depth and concentration in such a manner that the total number of ions or the total number of undissociated molecules in the path of the beam of light remains constant. This is easily done as follows: Let the concentration be denoted by c, the ratio of the number of dissociated molecules to the total number in solution by x, the depth of solution used by d; the number of ions in a cubic centimeter of the solution is then proportional to cx, and the number of undissociated molecules to $c(1 - x)$. To keep the number of ions in the path of the beam of light constant it is only necessary to keep the product cxd constant; and to keep the number of undissociated molecules constant the product $c(1 - x)d$ must remain constant. If the successive depths of solution to be used have been fixed arbitrarily, the required concentrations are determined in the following way: From tables giving the values of x for different values of c the products cx and

$c(1 - x)$ are calculated for all values of c. Two curves are then plotted, one between cx and c, the other between $c(1 - x)$ and c. Letting c_1, x_1, and d_1 represent the values of c, x, and d for the greatest concentration to be used, the values for any other concentration being represented by the same letters without subscripts, we have

$$c_1 x_1 d_1 = cxd, \qquad c_1(1 - x_1)d_1 = c(1 - x)d,$$

or, $$cx = \frac{c_1 x_1 d_1}{d}, \qquad c(1 - x) = \frac{c_1(1 - x_1)d}{d},$$

respectively.

The terms on the right are both known and hence the products cx and $c(1 - x)$ for any chosen value of d can be determined, and from the two curves the corresponding values of c may be read off directly.

Since more is known about dissociation than about association or solvation, it is only natural to try to see whether the observed changes in absorption can be explained by dissociation alone. If dissociation does not suffice, then we must conclude that other factors come in. The present work is devoted largely to a study of the absorption spectra of a large number of salts from the standpoint of dissociation.

Let us consider for a moment the kind of evidence obtained by the methods outlined, and what conclusions may be drawn from them. Consider first the possibility that an absorption band does not change in width or position with concentration, when the product of depth of layer and concentration is kept constant. The simplest explanation is that the absorption of the molecule and of the ions into which it breaks down on dissociation is the same. An excellent example of this type is furnished by the ultraviolet band of nickel sulphate; also by the more dilute solutions of neodymium and praseodymium chloride.

Let us now consider cases where we have deviations from Beer's law. Take first the possibility that an absorption band widens with dilution, when the product of concentration and depth of layer is kept constant. This would indicate either that the band is due to ions, or that the ions have stronger

absorption in the region considered than the undissociated molecules. By making a series of photographic exposures, keeping the number of ions in the path of the beam of light constant, we can decide between the two possible explanations. If the band now remains constant in width and position, it is most likely due to ions alone; if it narrows on dilution, it is due both to ions and molecules, but the ions have stronger absorbing power than the undissociated molecules; while if the band should widen with decrease in concentration, dissociation would in no way suffice to explain it.

The other case is where the band narrows with dilution, when the product of concentration and depth of layer is kept constant. If dissociation can account for this we must either have the undissociated molecules absorbing more strongly than the ions formed from them, or else the ions not absorbing at all. In the former case the band should widen with dilution when "undissociated molecules" in the path of the light are kept constant, while in the latter case the band would remain constant in width and position under the same conditions. If the band narrows with decrease in concentration when the number of undissociated molecules is kept constant, dissociation alone can not possibly explain the facts. An example of this case is furnished by the ultraviolet absorption of most copper salts in aqueous solution.

A case often met with in the present work is where a band narrows with dilution when the product of concentration and depth of layer is kept constant, but widens when the number of undissociated molecules is kept constant. This deserves further consideration, as dissociation may or may not be able to account for it, depending on the nature of the change in the band. The case was discussed by E. Müller, who showed that by measurements with a spectrophotometer of the extinction coefficient at various concentrations, we may determine whether Beer's law holds for each one of the three absorbers in a solution of an electrolyte, even when these have quite different powers of absorption. Work on this point is now in progress with the solutions showing the effect just spoken of, and the results will be published shortly.

Another interesting method of studying absorption spectra is to keep both concentration and depth of layer constant, and to vary the temperature. Much work of this kind has already been done by Hartley and others, and a similar investigation is now in progress in this laboratory. As is well known, change of temperature has only a small effect on the dissociation, hence we may say that when the temperature is varied the dissociation remains nearly constant. The spectrum of some solutions, however, undergoes very great changes; for example, solutions of cobalt chloride which are red at room temperatures become blue when the temperature is elevated sufficiently; and according to Donnan and Bassett solutions of the same salt in ethyl alcohol, which at ordinary temperatures are blue, turn red when cooled down to −75° C. This effect, which involves the appearance or disappearance of a complicated set of absorption bands in the red, can evidently not be accounted for by dissociation, since it is observed when the dissociation is known to change but very slightly.

In the present work considerable attention has been given to solutions in nonaqueous solvents, such as methyl alcohol, ethyl alcohol, and acetone, as well as to solutions in mixtures of these solvents with water. In this part of the work great care has been taken to have both the salts and solvents as free from water as possible, and this is of fundamental importance, as is shown by the spectrograms of solutions of neodymium chloride in mixtures of alcohol and water, where it appears that the change in the spectrum produced by 1 per cent or less of water may easily be detected.

The question of the effect of the solvent comes up in this connection, and this in turn involves the more general question as to the condition of a molecule of a dissolved substance in any solvent whatsoever. Does it form some kind of a compound with the solvent, or does it move about freely in the solvent without materially changing its nature? Kundt's law, which states that the effect of the solvent upon absorption is simply to shift the position of the absorption bands, these being located nearer the region of long wave lengths the greater the dispersion of the solvent, seems to imply that the molecule

of the dissolved substance exists in the free state in solutions. If this view be taken, then the effect of the solvent should not be very great, especially if solutions in solvents having similar optical properties are compared If, on the other hand, a salt, when it goes into solution, always forms some sort of a compound with the solvent, we might expect to find that solution produces radical differences in the absorption.

It is evident that a study of the absorption spectra of a salt, when dissolved in various solvents, ought to bring out many points of interest bearing upon the question of the nature of solutions.

Apparatus.

For visual examination of solutions a small, direct-vision, grating, pocket spectroscope was always at hand, and was found very useful for the purpose of determining what particular range of concentrations it was desirable to work with. Judging from the color of the solution as seen by the unaided eye was found to be very unsatisfactory, since many solutions have very wide absorption bands which may give the solution quite a decided tint, even when the absorption is so feeble that it would be almost impossible to obtain a satisfactory photographic record of it. On the other hand, when solutions have narrow, intense absorption bands, like those of the salts of the rare earth metals, the solution may show practically no color to the unaided eye, and still the absorption bands may be quite intense as seen in the spectroscope.

For photographing the spectra, the vertical grating spectrograph used by Jones and Uhler was employed. In its original form as used by them, films 2.5 by 7 inches, on which the spectrum from λ 2000 to λ 6300 could be registered, were employed.

In the present work it was decided to remodel it so as to allow the whole spectrum from λ 2000 to λ 7600 to be photographed, and accordingly the camera and the camera end of the box were enlarged so as to hold films 2.5 by 9 inches. Owing to the fact that the grating has only 10,000 lines to the inch, it was not possible to add the extra 2 inches to the

red end of the camera. If this could have been done, it would
have left the grating axis very near the middle of the spec-
trum. The 2 inches were actually added to the ultraviolet
end, which necessitated turning the grating axis farther away
from the slit, thus placing it in a point of the spectrum some
little distance beyond the visible violet. The spectrum is,
however, near enough to normal, even at the extreme red
end, to make any correction unnecessary, unless measurements
of a very high degree of accuracy are required.

For holding the aqueous solutions, the cell illustrated in
Fig. LXVI.,[1] page 172, of "Hydrates in Aqueous Solution,"
was employed throughout, while for nonaqueous solvents
the cell shown in Plate XXII.[2] of the same work was used.

Photographic Material, Etc.

It was at first decided to use films coated with the pan-
chromatic emulsion made by Wratten and Wainwright, of
Croyden, England, as this emulsion has been found to be
very uniformly sensitive to light of all wave lengths between
λ 2000 and about λ 7400. The makers, however, did not
succeed in producing a satisfactory film in time for the pres-
ent work, and hence it was necessary to use the Seed L-ortho-
film for the region from λ 2000 to about λ 6000, and to make
a separate exposure for the red end of the spectrum, using for
this purpose Wratten and Wainwright panchromatic glass
plates, cut to such lengths (4 to 4.5 inches) that the curva-
ture of the focal plane would not introduce any appreciable
difficulty. This method very nearly doubled the time and
work necessary to make the spectrograms, as two separate
sets of exposures had to be made with each set of solutions.
It also made it very difficult to get the two negatives of such
intensities that they would match satisfactorily, owing not
only to the different absolute sensibility of the two emulsions
to light of a given wave length, but also to the different rates
at which the photographic blackening increases with time for
the two emulsions.

[1] Cf. This Journal, **37**, 141 (1907).
[2] Cf. *Ibid.*, **37**, 247 (1907).

The developer used throughout was a concentrated hydro-quinone solution made up according to Jewell's formula.[1]

Sources of Light.

The most satisfactory source of light for the region of the spectrum lying between the extreme red and the beginning of the ultraviolet is the Nernst lamp, as it is brilliant enough to bring the necessary time exposure down to about a minute, and is, of course, perfectly continuous and steady. In the ultraviolet it has been shown that its action decreases rapidly with the wave length, ceasing practically at about λ 3200. For this region, then, some spark spectrum must be used. The cadmium-zinc spark used by Jones and Uhler is fairly satisfactory, being especially strong in the extreme ultraviolet, but it has the disadvantage of having a limited number of very intense lines on a rather faint, continuous background. It was hoped that some spark spectrum could be found having a very large number of lines, but without any lines of very great intensity.

A reference to published tables of the spectra of the elements showed that tungsten, molybdenum, and uranium all satisfy this requirement. Each of these has so many lines, and these so closely packed, that with an instrument of moderate dispersion the spectrum ought to be nearly continuous. The problem was to make spark terminals of these substances which could be used satisfactorily. The metals not being easily obtainable, the following plan was tried: Sheet carbon about 3 mm. thick was cut into pieces about 1 cm. by 4 cm. and dipped in concentrated solutions of ammonium molybdate, or uranium nitrate; a suitable solution of a tungstate was not tried. These pieces of carbon were then heated to redness in a Bunsen flame and again quickly immersed in the solution, the process being repeated two or three times. Some pieces were also treated with solutions of salts of iron, copper, and cobalt, and others were treated with two or more of the solutions in succession. The spectra of these carbon terminals showed the lines of the metals with which they were

[1] Astrophys. J., **1900**, 240–243.

treated almost as well as terminals of the metals themselves; but in the case of iron, copper, or cobalt the cyanogen bands were also observed. With molybdenum and uranium, however, the cyanogen bands did not appear, the merest trace of the λ 3883 band being detected. The uranium spectrum is almost continuous with the dispersion employed, but its intensity falls off very rapidly from λ 3000 toward the ultraviolet. The molybdenum spectrum, although not so nearly continuous, is much richer in ultraviolet, being quite strong as far as λ 2300

Curiously enough, if a pair of carbon terminals is treated with molybdenum and also with one or more of the other metals, very little except the molybdenum spectrum is seen. Uranium, however, seems to increase the intensity of the continuous background somewhat, and hence the terminals finally used were prepared by dipping them twice in the molybdate solution and then three times in the solution of uranium nitrate.

It was also found that the terminals charged with various metals wore away at quite different rates when the spark was passed. Those dipped in a solution of copper wore away at the rate of a millimeter or more per minute, while those treated with molybdenum could be used for hours without appreciable wear. The character of the spectrum given by these molybdenum-uranium terminals may be seen from any of the plates reproduced in the following sections which do not show complete absorption in the ultraviolet.

The coil used to produce the spark was a large Röntgen X-ray coil, through the primary of which was passed an alternating current of from 5 to 8 amperes, 60 cycles; and across the secondary terminals was shunted a capacity of about 0.011 microfarad. The spark used was about a centimeter in length, and was placed about 15 cm. above the slit, the direction in which the spark passed being perpendicular to the length of the slit. By this arrangement the grating received light from all parts of the spark at the same time. In order to produce a uniform photographic strip of the proper width, it was necessary to keep the spark terminals moving in a direc-

tion parallel to the length of the slit, which was done by hand, a suitable stand being used. Care was taken to move the sparkholder always at the same rate, namely, a to-and-fro motion in about 4 seconds, which insured equality in times of exposure for the different strips of the spectrograms. The intensity of the spark undoubtedly varied somewhat, due to fluctuations of the voltage impressed upon the primary terminals of the coil; but this was found to be so small that no provision was made for regulating it. The Nernst filament is, however, so sensitive to slight changes in voltage that a variable resistance was placed in series with it; by regulating this the current was always kept at 0.8 ampere during an exposure.

Making a Spectrogram.

In making a spectrogram consisting of seven photographic strips with a comparison spectrum, the following was the usual sequence of operations: Seven separate solutions were made up, the quantity of each being usually 25 cc. The cell to be used having been cleaned and dried, was filled to the required depth with the most concentrated solution of the series, and the quartz plates limiting the depth of the solution adjusted to parallelism. The exposure to the Nernst lamp was then made, the current being kept at 0.8 ampere by hand regulation of the variable resistance in series with it. The usual time of this exposure was 1 minute. An opaque screen covering up the visible spectrum as far down as λ 4000 was then interposed between the grating and the photographic film, and the exposure to the light of the spark in the ultra-violet was made. The duration of this exposure was usually 2 minutes. The photographic film was then moved a distance of 6.5 mm. into the proper position for the next exposure. The cell was emptied and rinsed out with a few drops of the next solution, and the series of operations repeated for the second strip, and so on. It was always found advisable to clean the slit jaws after exposure, and also to see that the image of the Nernst filament fell in the proper position on the slit.

After the film had been exposed and the comparison spark spectrum impressed, it was necessary to make a series of exposures on a panchromatic plate for the red end of the spectrum, using the same set of solutions. No exposure to the spark was made in this set except for the narrow comparison strip. As the extreme end of the plate was at about λ 7600, λ 3800 of the second order would overlap the first order here. Accordingly an absorbing screen was always used in making the exposures for the red end of the spectrum. This screen consisted of two glass plates separated by a layer of Canada balsam a little less than a millimeter thick. It absorbed all radiations of shorter wave length than λ 3900.

The scale accompanying the spectrograms in the following chapters was made by photographing an ordinary paper scale. Several photographs were made, the distance between the paper scale and the lens of the camera being varied slightly from exposure to exposure. The negative which fitted the majority of spectograms best was selected and used throughout. Absolute accuracy is not to be expected, owing to the fact that both photographic films and the paper on which prints from these were made contract more or less in drying, and different films or papers contract differently. λ 5000 on the scale was always placed in coincidence with the corresponding wave length on the photographic strips; the correction for the ends of the spectrograms differs slightly for the different plates, but never amounts to more than about 25 or 30 Ångström units.

SALTS OF COBALT.

Jones and Uhler,[1] in their work on the absorption spectra of salts of cobalt and copper, discussed a number of the more important papers dealing with cobalt, so that it is necessary only to make brief reference to them here.

Babo[2] observed a number of the color changes produced in cobalt salts by change in temperature, or by addition of a de-

[1] Publication No. 60, Carnegie Institution of Washington.
[2] Jahresb., **1857,** 72.

hydrating agent. Similar observations were made by Gladstone[1] and Schiff.[2]

Bersch[3] proposed the view that there are two modifications of the compound $CoCl_2.6H_2O$—the one red and the other blue—which would thus account for the color changes in cobalt salts with rise in temperature.

Tichborne[4] would also account for these color changes on the basis of hydration, and Vogel's[5] work pointed in the same direction.

The investigations of Russell[6] on the absorption spectra of solutions of cobalt salts is important. He worked under various conditions, such as with the fused salt, with its solution in concentrated hydrochloric acid, and with solutions in the various alcohols and glycerol. He also studied the effect of changes in temperature on the absorption spectra. He concluded, as the result of all of his work, that the color of the aqueous solutions was due to the presence of hydrates.

Potilitzin[7] showed that the conclusion of Bersch, that there are two modifications of the compound $CoCl_2.6H_2O$, is an error, and that the formation of blue cobalt chloride from the red modification is always a dehydration phenomenon.

Etard[8] studied the color changes and also the solubility curve of cobalt chloride and iodide, and showed that the sudden changes in the direction of the solubility curves indicated the existence of various hydrates of these salts. He also studied the changes in the absorption spectra of cobalt chloride with changes in temperature.

Engel[9] does not believe that any general theory can be advanced to account for the changes in color of cobalt salts, but thinks that the blue color is often due to the formation of double compounds. The blue color of a hot, saturated solution of cobalt chloride, he believes, is due to a double com-

[1] J. Chem. Soc., **10**, 79 (1859).

[2] Ann. Chem. (Liebig), **110**, 203 (1859).

[3] Sitzun. Wien [2], **56**, 726 (1867).

[4] Chem. News, **25**, 133 (1872).

[5] Ber. d. chem. Ges., **8**, 1533 (1875); **11**, 913 (1878); **12**, 2313 (1879).

[6] P. Roy. Soc., **32**, 258 (1881); Chem. News, **59**, 93 (1889).

[7] Ber. d. chem. Ges., **17**, 276 (1884); Bull. Soc. Chim. [3], **6**, 264 (1891).

[8] Compt. rend., **131**, 699 (1891); **120**, 1057 (1895).

[9] Bull. Soc. Chim. [3], **6**, 239 (1891).

pound between the salt and the hydrochloric acid liberated as the result of hydrolysis.

Wyrouboff[1] and Le Chatelier[2] show that Engel's view is untenable.

W. N. Hartley,[3] in his elaborate investigations of absorption spectra, has included a number of salts of cobalt. His experimental work consisted in observing and photographing the spectra of a large number of solutions of chlorides, bromides, iodides, nitrates, etc., of a fairly large number of metals, including cobalt. Some of the more interesting and important conclusions at which he arrived, stated nearly in his own words, are the following:

When a definite crystalline hydrate is dissolved in a non-aqueous solvent, upon which it does not act chemically, the molecules of the salt remain unchanged in chemical composition.

In a series of anhydrous salts which do not form definite crystalline hydrates, the effect of rise in temperature up to 100° C. does not produce any alteration in their absorption spectra other than that which results with substances which undergo no chemical change with such rise in temperature. The change in question is usually an increase in the intensity of the absorption, or a slight widening of the absorption bands.

Crystallized hydrated salts dissolved in a minimum amount of water at 20° C. undergo dissociation when the temperature is raised. The extent of the dissociation may proceed as far as complete dehydration of the compounds, so that more or less of the anhydrous salt may be formed in the solution.

The most stable compound that can exist in a saturated solution at 16° C. or 20° C. has not always the same composition as the molecule of the crystallized solid at the same temperature, since the solid may undergo a partial dissociation from its water of crystallization when the molecule enters into solution. When a saturated solution of a colored salt suffers a great change in color or any remarkable change in

[1] Bull. Soc. Chim. [3], **6**, 3 (1891).

[2] *Ibid.* [3], **6**, 84 (1891).

[3] Trans. Roy. Dub. Soc. [2], **7**, 253–312 (1900); J. Chem. Soc., **81**, 571 (1902); **83**, 221 (1903).

its absorption spectrum upon dilution, the dilution is always accompanied by marked evolution of heat.

Hartley[1] closes his paper on "The Absorption Spectra of Metallic Nitrates" with the following significant paragraph:

"The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound into ions, but only a dissociation of such a character that the molecule is shown to consist of two parts, the movements of the one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation such as may be brought about by electrolysis or by static electricity, and, in some instances, by photographic action."

Ostwald[2] thinks that the red color of solutions of salts of cobalt is due to the cobalt ions.

The paper of Donnan and Bassett[3] should be especially mentioned in connection with the changes in color of cobalt salts. After citing a number of well-known facts, and adding a fairly large number of interesting new ones, they came to the conclusion that the blue color of solutions of cobalt salts is due to the formation of complex anions containing cobalt. Some of the evidence which they furnish merits very careful consideration in this connection.

Hartley[4] takes issue with the conclusions reached by Donnan and Bassett, interpreting the facts cited or discovered by them in terms of hydration and dehydration.

A fairly large number of salts of cobalt has been brought within the scope of this investigation. Thus, plates have been obtained for cobalt chloride in water—to test Beer's law; cobalt chloride in water—number of ions in the path of the beam of light constant; cobalt chloride in water—molecules constant; cobalt chloride in methyl alcohol—Beer's law;

[1] J. Chem. Soc., **83**, 245 (1903).
[2] Grundlinien d. anorg. Chem., p. 620.
[3] J. Chem. Soc., **81**, 939 (1902).
[4] *Ibid.*, **83**, 401 (1903).

cobalt chloride in ethyl alcohol—Beer's law; cobalt chloride in acetone—Beer's law; cobalt chloride in methyl alcohol to which water is added; cobalt chloride in ethyl alcohol to which water is added; cobalt chloride in acetone to which water is added; cobalt bromide in water—Beer's law; cobalt bromide in water—molecules constant; cobalt bromide with calcium bromide; cobalt bromide in methyl alcohol—Beer's law; cobalt bromide in ethyl alcohol—Beer's law; cobalt bromide in acetone—Beer's law; cobalt bromide in methyl alcohol to which water is added; cobalt bromide in ethyl alcohol to which water is added; cobalt bromide in acetone to which water is added; cobalt nitrate in water—Beer's law; cobalt nitrate in water—molecules constant; cobalt sulphate in water— Beer's law; cobalt sulphocyanate in water—Beer's law; cobalt sulphocyanate in water—molecules constant; cobalt acetate in water—Beer's law.

In all twenty-three complete plates, all of which are given in the Carnegie Publication,[1] were made with salts of cobalt. Only three are reproduced in this paper.

Cobalt Chloride in Water—Beer's Law (See Plate I., A and B).

In both A and B, the strip corresponding to the most concentrated solution is adjacent to the numbered scale. The concentrations of the solutions used in making set A were 2.5, 1.88, 1.25, 0.83, 0.58, 0.42, and 0.31, respectively; the corresponding depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm. The concentrations used in making set B were 0.83, 0.63, 0.42, 0.276, 0.192, 0.139, and 0.104; the depths of cell were the same as in set A. The exposures to the red end of the spectrum were omitted in this case, inasmuch as observations with the direct-vision spectroscope showed that the solutions, at least in such thicknesses of layer as were employed, were perfectly transparent from the beginning of the orange to the end of the red. The most concentrated solution in layers of 2 cm. or more showed faint traces of bands in the orange and red, but in layers of a few millimeters thickness these were, of course, quite invisible.

[1] Carnegie Institution Publication, No. 110.

Plate I.
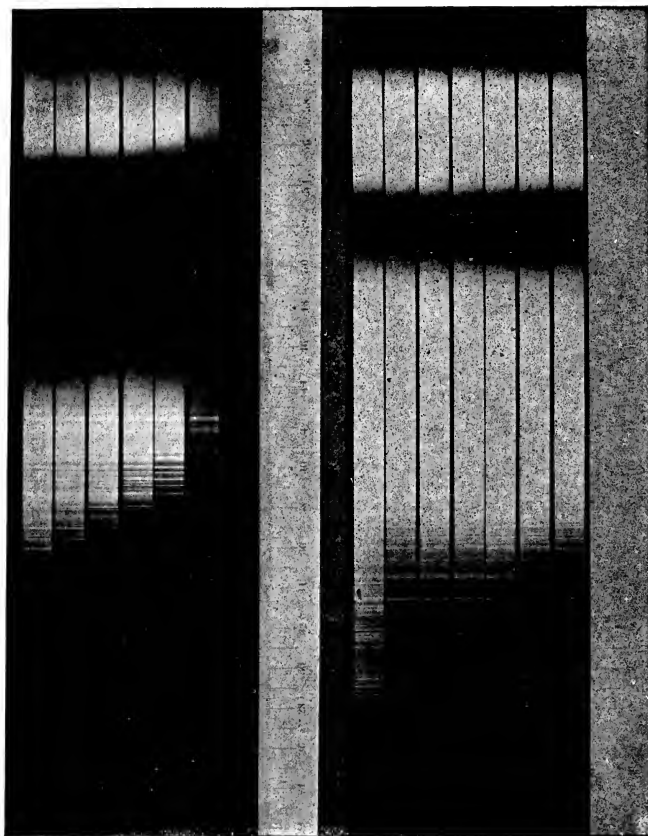
A

B

The spectrogram shows three regions of absorption; one in the green, middle near λ 5200; one in the ultraviolet, with its middle near λ 3300; and one in the extreme ultraviolet. The strips corresponding to the four most concentrated solutions of set A show only one absorption band in the ultraviolet, but the strip corresponding to the fifth solution shows transmission between λ 2800 and λ 3000, and absorption from λ 3000 to λ 3500, thus making it very evident that there are two regions of absorption. The strips corresponding to the three most concentrated solutions of set B also show very plainly the existence of the band at λ 3300, although the absorption is not complete even at the middle of the band. In the fourth strip of B, corresponding to a concentration of 0.276 and depth of cell equal to 9 mm., practically all trace of the band has disappeared, the spark spectrum appearing to shade off uniformly from λ 3600 to λ 2650, where it ends.

It will be noticed that the intensity of the spark spectrum in the region λ 2900 is greater for the strips near the numbered scale than for the fourth, fifth, and sixth strips. This is due partly to a gradual decrease in the intensity of the spark itself while the spectrogram was being made, produced by a gradual fall in potential of the source of alternating current operating the coil. That the effect is real, however, is shown by another plate, where a similar decrease in transmission at λ 2900 with dilution is recorded, and where the intensity of the spark was constant or very nearly so throughout. The increased intensity of the seventh strip of Plate I, B is due to the fact that before making the exposure the potential was readjusted to its original value.

The absorption in the extreme ultraviolet decreases regularly with dilution, the strip corresponding to the most concentrated solution in set B transmitting as far as λ 2650, while that corresponding to the most dilute solution shows transmission a little below λ 2500.

In set A the band in the green narrows quite rapidly at first, then more slowly with dilution. In set B it remains very nearly constant, especially in the strips corresponding to the more dilute solutions.

The facts brought out by the spectrogram may be summed up briefly as follows: When the product of concentration and depth of absorbing layer is kept constant, the absorption band in the green remains constant, except in very concentrated solutions, where it narrows somewhat with dilution; the one-sided, extreme ultraviolet absorption decreases with dilution, while the band having its center near λ 3300 narrows very rapidly with dilution, disappearing entirely when a concentration of about quarter normal is used in a layer about 1 cm. in depth. In the region λ 2800 to λ 3000 there is remarkable transparency in solutions having a concentration about half normal. This transparency decreases somewhat with dilution to about one-tenth normal.

A comparison between this plate and Plate II. in the work of Jones and Uhler, already referred to, reveals a remarkable difference in the ultraviolet. The four strips nearest the comparison spectrum of their plate correspond to concentrations of more than 2.0 normal, with a depth of absorbing layer of 0.67 cm., and yet the absorption in the region λ 3000–λ 3500 is not very great. It might at first sight seem probable that the absorption band in this region was produced by some impurity in the cobalt chloride used. But this is improbable, since the salt from which were obtained the solutions used by Jones and Uhler and those used in the present work came from the same sample of material. Besides, Plate XXIII., in "Hydrates in Aqueous Solution," shows that the solution of the cobalt chloride used by Jones and Uhler, when dissolved in methyl alcohol, exerts strong absorption in the ultraviolet, while Plate I. of the present work indicates only faint absorption in this region, although the concentrations, depth of cell, etc., used in the two cases, did not differ materially; hence, it is evident that it is not a question of the presence of an impurity. The probable explanation is that the discrepancy is due to a difference of temperature.

It is well known that the absorption of cobalt salts in solution is greatly affected by even slight changes in temperature, and if the λ 3300 band is especially sensitive, such variations of temperature as occur in the laboratory on different

Plate II.
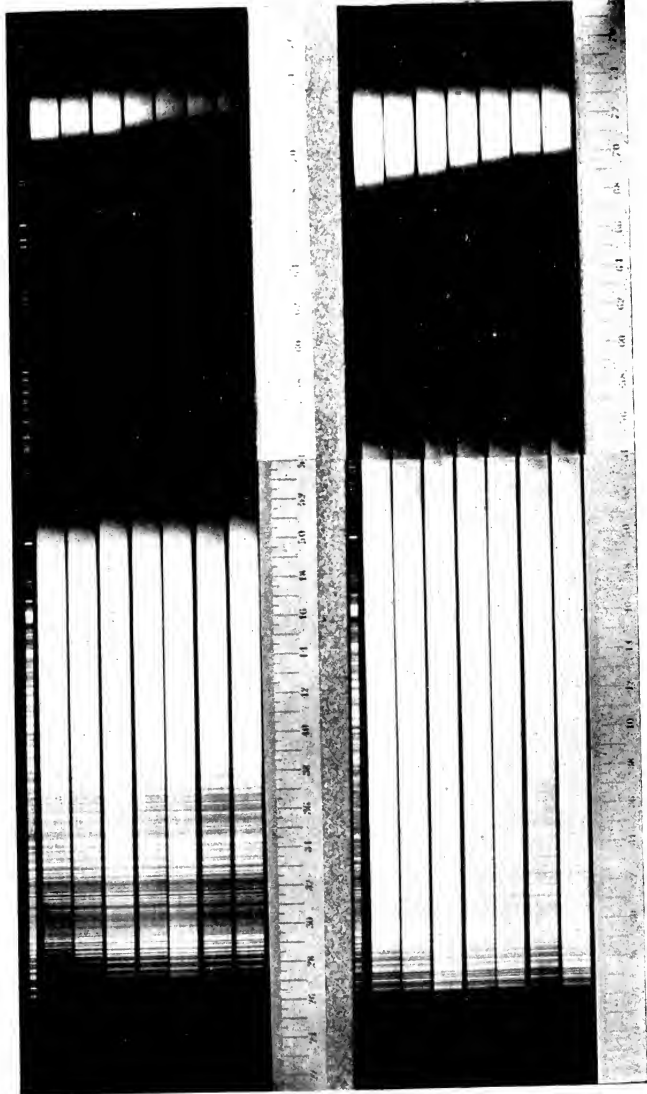
A.

B.

days might be sufficient to account for the change in the spectrum observed. No data are at hand, however, giving the change of absorption in the ultraviolet produced by change of temperature, and hence this point will have to remain unsettled until the work now in progress shall have supplied the data for the absorption band in question.

Cobalt Chloride in Ethyl Alcohol—Beer's Law (See Plate II.).

The concentrations of the solutions used in making the negative for A were 0.15, 0.126, 0.104, 0.086, 0.071, 0.060, and 0.050; the corresponding depths of cell were 8, 9.5, 11.5, 14, 17, 20, and 24 mm., respectively. For B the concentrations were 0.060, 0.050, 0.042, 0.034, 0.028, 0.024, and 0.020, the corresponding depths of cell being the same as those used in making set A.

The color of the solutions, as seen in the bottles, was deep blue for the most concentrated, changing to a light greenish-blue for the most dilute. The general absorption observed in the concentrated solutions in methyl alcohol was quite absent in the ethyl alcohol solutions, so that in making the negatives for both A and B the slit was adjusted to a width of 0.01 cm. and the exposures to the Nernst lamp and spark were 1.5 and 3 minutes, respectively.

The spectrogram shows a region of absorption in the extreme ultraviolet which narrows regularly with dilution; the limits of transmission for the strips corresponding to the most concentrated and most dilute solutions of set A are λ 2670 and λ 2630, respectively, while for set B they are λ 2580 and λ 2550.

The negative for set A also shows two absorption bands in the ultraviolet, having their centers approximately at λ 3100 and λ 3600. These bands are undoubtedly identical with those already noted in the same region for the solution in methyl alcohol. One difference, however, is to be noted. The bands in the ethyl alcohol solutions are somewhat more intense, in spite of the fact that the concentration of the colored salt is smaller, and they also disappear much more slowly with dilution.

The absorption in the green is very much fainter in ethyl alcohol than in methyl alcohol, and measurement of the position of the center of the band indicates that it is located a trifle nearer the red in the former case. The position of the center was found to be at λ 5280. The band remains constant in width and position with dilution; A shows a region of intense absorption in the yellow, orange, and red, which narrows somewhat with decrease in concentration; the limits of transmission for the most concentrated solution are λ 5500 and λ 7170, and for the most dilute, λ 5500 and λ 7060.

In B the absorption in this region of the spectrum is less intense, especially for the more dilute solutions, which show faint transmission throughout the band. The red edge of the band for the most concentrated solution is at λ 6970, while for the most dilute solution it is at λ 6800; the wave lengths given correspond to the limits of transmission, as indicated by the photographic blackening of the negative. The strips for the more dilute solutions of set B show faint traces of bands, which appear to correspond approximately in position to the bands noted in the analogous solutions in methyl alcohol. The bands at λ 5910 and λ 6050 show only faintly, and they both appear much less clearly defined than in the methyl alcohol solutions.

Cobalt Chloride in Ethyl Alcohol to which Water is Added (See Plate III.).

The concentration of cobalt chloride throughout was 0.088. The percentages of water, beginning with the solution used in making the strip nearest the numbered scale, were 0, 1, 2, 3, 4, 5, 5.5, 6, 6.5, 7, 7.5, 8, 9, 10, 11, and 12. The duration of the exposures to the Nernst lamp and the spark was $1^1/_6$ and 3 minutes, respectively; the slit was adjusted to a width of 0.01 cm. The common depth of absorbing layer was 2.0 cm.

In the four solutions containing the least amount of water the bands at λ 3100 and λ 3600 are very intense, making the absorption for the solution in pure ethyl alcohol complete from λ 3800 to the end of the ultraviolet. The bands, how-

Plate III.

ever, disappear rapidly on addition of water, so that in the strip corresponding to 6 per cent of water they can hardly be noticed. This strip transmits light as far out at λ 2600, while on the strip for the solution containing 12 per cent of water transmission extends to λ 2475.

The band in the green behaves very much the same as it does in methyl alcohol, being, however, somewhat fainter in ethyl than in methyl alcohol. Its middle for the solution containing 12 per cent water is at λ 5200. For the solution in pure ethyl alcohol it is not possible to determine its middle, as it unites with the strong absorption band in the orange and red, this solution showing complete absorption from about λ 4930 to λ 7200.

The absorption band in the red narrows very rapidly with addition of water. Its limits for the solution containing 3 per cent of water are λ 5750 and λ 7000. In the strips corresponding to the solutions containing from 5 to 7.5 per cent of water, the band breaks up into a rather complicated spectrum. Absorption bands may be noticed having centers at λ 5910, λ 6060, λ 6240, λ 6400, and λ 6700. Of these, the last is the strongest and widest. The one at λ 6400 is very faint, the one at λ 5910 a little more intense; while those at λ 6060 and λ 6240 are fairly intense, comparing favorably with the bands in the same region seen in the corresponding methyl alcohol solution.

Referring to the description of the negatives from which Plate II. was made, it will be recalled that, although the absorption in the red showed signs of breaking up into finer bands, these did not appear very distinctly. Indeed, the only ones that could be made out were those at λ 5910 and λ 6060. The water added to solutions of cobalt chloride in ethyl alcohol must hence play an important part in the development of these bands, and it is barely possible that the faint development of the bands noted in Plate II. may have been due to the slight traces of water which it is impossible to remove from ethyl alcohol, or which might have found its way into it in the process of pouring the solution into the cell and exposing this in the spectrograph. It is probable that the ac-

tivity of water in producing changes in the absorption spectrum depends not upon the percentage relation of water to alcohol, but upon that of water to amount of salt in a given volume of the solution. This was found to be so for solutions of neodymium salts in mixed solvents, which will be discussed in the section dealing with the rare earths. If this rule also applies to cobalt salts, we may say that since 5 per cent of water produces a fair development of the bands in a solution of concentration 0.088, it would require only about 1 per cent of water to do the same in the most dilute solution used in making the negative for Plate II., the concentration of which was 0.02. The bands there were much less clearly developed, which, if they were caused by water, would indicate the presence of water to an amount of about 0.5 per cent, which is well within the range of probability.

It is not at all improbable that the absorption bands in the red region of the spectrum, shown by solutions of cobalt salts dissolved in ethyl alcohol, may be used as a delicate test for the presence of water in the solvent.

General Summary of Results with Cobalt Salts.

We shall consider the aqueous solutions first, since they are the simplest from the standpoint of the absorption spectra. With two exceptions, all of the solutions studied at room temperatures and with such depths of absorbing layer as were employed, show only two regions of absorption, one in the ultraviolet and one in the green. The exceptions, both of which show some absorption in the red, are the concentrated solutions of the sulphocyanate, and the solutions of cobalt bromide to which large amounts of calcium bromide had been added.

Let us first consider the absorption in the ultraviolet. Solutions of all the salts studied, except the sulphate, have a region of so-called one-sided absorption, which cuts off more or less of the ultraviolet end of the spectrum, depending upon the salt used. In all cases the band narrows with dilution when the conditions for Beer's law obtain, but tends to remain approximately of constant width when molecules are kept con-

stant. In the bromide and nitrate the band is constant with molecules constant. This indicates that the absorber which is responsible for this band is in every case the undissociated molecule, and to account for the deviations from constancy in the band when the number of absorbers is kept constant, we may assume that the molecules in concentrated solutions associate to some extent, and that their absorbing power is thereby increased; or we may assume that with increasing dilution they become more and more hydrated, and that this decreases their absorbing power. A choice between these two explanations cannot be made without a further study of the subject.

In addition to the one-sided ultraviolet band, cobalt chloride has a band at λ 3300, which disappears rapidly with dilution even when molecules remain constant. This band seems to increase in intensity very rapidly with rise in temperature. We cannot very reasonably ascribe this band to the undissociated molecules as such, since it not only narrows rapidly but entirely disappears when these are kept constant. To explain it we must look, therefore, either to association or to hydration. It may be remarked here that by association we do not mean simply a grouping together of similar particles, but also a grouping together of such parts as molecules and ions, or aggregates of molecules and ions, etc. The term association, therefore, includes the complex anions assumed to exist by Donnan and Bassett. Both association and hydration are known to diminish with rise in temperature (except in Donnan and Bassett's complex anions); with increasing concentration at a given temperature association is known to increase while hydration decreases. In a fairly dilute solution the amount of association is perhaps negligible. If we then assume that the λ 3300 band is due to some aggregate, this would explain its disappearance on dilution, since this process destroys the aggregate. But raising the temperature also destroys the aggregate without, however, causing the absorption band to disappear. The fact is that it becomes more intense as the temperature rises. It seems, therefore,

rather difficult to assume that it is due to aggregates, at least to aggregates which are not abnormal in their behavior.

If we assume that the band is due to some *relatively simple hydrate* the facts are at once accounted for, since with rise in temperature complex hydrates break down into simpler ones. Also with increase in dilution more and more complex hydrates are formed, which would also cause the band to disappear.

The green band appears in all aqueous solutions, although with various intensities and apparently in somewhat different positions. The change in position is inappreciable in the case of dilute solutions, and with concentrated solutions it depends entirely upon whether the band widens symmetrically or not. In general, it widens perhaps a trifle more towards the violet, especially at first. A very slight amount of general absorption will shift the apparent center of an unsymmetrical band, and this is perhaps the explanation of the slight variation in the position of the center of this band in concentrated solutions of different salts.

The intensity of the band, as indicated by its width on the photographic plate, is more interesting. For if it is due to the cobalt cation as such, it ought to have a greater intensity in solutions which are strongly dissociated than in slightly dissociated solutions, concentration and depth of layer being constant.

Our spectrograms of cobalt solutions show the following: For solutions having a concentration of 2 normal or more, the salts arranged in the order of increasing intensity of the green band are: nitrate, bromide, chloride, sulphocyanate. For dilute solutions (concentrations of about 0.1 or 0.2 normal) the order is: bromide, chloride, nitrate, sulphate, acetate, sulphocyanate. Arranged in the order of increasing dissociation the salts would be: acetate, sulphate, sulphocyanate, nitrate, chloride, bromide. This is just the opposite of the order of increasing intensity of the green band, if we leave out the sulphocyanate. It is very evident, therefore, that something besides the cobalt cation must play a part in the production of this band.

It has been shown that when the concentration of the sulphate is varied from 0.65 to 0.06 the width of the band does not vary, provided the light is made to pass through such depths of the solution that the products of concentration and depth remain constant; it follows, therefore, that in this case the absorption is simply proportional to the number of cobalt atoms in the solution, and independent of whether these exist as ions, or combined with SO_4, as molecules, or as parts of the various aggregates or hydrates that we may assume to exist in the solution. The same is approximately true for the nitrate solutions, although in this case there is a slight narrowing of the band, indicating that the absorbing power of the various "absorbers" is not the same. In general, the simplest explanation of the green band is to assume, as we have just done, that the cobalt atom, no matter what it is combined with, has the power of absorbing green light, the intensity of the absorption depending, however, upon the nature of the combination.

Aqueous solutions show little or no absorption in the red unless they are very concentrated, or are at a high temperature, or relatively large amounts of such substances as hydrochloric acid, calcium chloride, or aluminium chloride, etc., are added to them. Whether the absorption produced by these different methods is the same or not for any given salt cannot yet be answered definitely. We have pointed out that the absorption of a solution of cobalt bromide to which a large amount of calcium bromide is added is similar *but not identical* with that of a solution of the chloride of cobalt to which a large amount of calcium chloride had been added. The work of Jones and Uhler ("Hydrates in Aqueous Solution") indicates that the absorption of cobalt chloride, when "dehydrated" with calcium chloride, aluminium chloride, or calcium bromide, is the same, but that this differs somewhat from the absorption of very concentrated solutions of cobalt chloride alone. In the latter case only three of the five bands were seen, and these were located nearer the red end of the spectrum, but the "displacement" was different for different bands, amounting to 170 A. U. for the least refrangible, and to 115 A. U. for the most refrangible.

The entire absence of this red absorption in solutions of moderate concentration shows at once that it cannot be accounted for by the simple theory of dissociation, according to which there should be present only ions and molecules. The fact that the absorption does appear in *very* concentrated solutions naturally suggests that it may be due to aggregates of molecules, but this view is not tenable since the absorption increases with rise in temperature. The most reasonable explanation, and the one that best fits the facts, is that it is due to some relatively simple hydrate of the molecule. The conditions which favor the formation of a "simple" hydrate are high temperature, or great concentration, or the addition of large amounts of some dehydrating agent to a moderately concentrated solution, and in all of these cases the absorption in the red appears. That this explanation is the correct one is also made probable by the work of Russell on the absorption of the various dry salts of cobalt. The anhydrous salts also show absorption in the red, as do also the simple hydrates, while hydrates containing 6 molecules of water exert no absorption in this region of the spectrum.

In nonaqueous solvents only the chloride and bromide have been studied. The chloride, which in aqueous solutions showed an absorption band near λ 3300, has in the alcoholic solutions two bands, one at λ 3100 and the other at λ 3600. These bands behave very much like the λ 3300 band in the aqueous solution, disappearing quite rapidly with dilution. They are most likely due to some relatively simple solvate. A study of the change of absorption with temperature will undoubtedly throw some light on this point.

The green band is present in all the nonaqueous solutions studied, although its intensity in the acetone solutions is so small that very deep layers of solution were necessary in order to make even a trace of it visible. This is exactly what we should expect if the cobalt atom, no matter with what it is associated, absorbs green light to some extent. The intensity of the band diminishes as we pass from solutions in methyl alcohol to those in ethyl alcohol and acetone, but so do the concentrations; hence, as in aqueous solutions, the intensity

of the band may be said to be approximately proportional to the concentration.

In the red the absorption is much more intense in the non-aqueous than in aqueous solutions, the intensity for equal concentrations increasing very rapidly as we pass from methyl alcohol to ethyl alcohol to acetone. The structure of the band differs materially in the different solvents, as has been pointed out in the description of the spectrograms. With dilution it narrows rapidly in methyl alcohol, more slowly in ethyl alcohol, and remains constant or nearly so in acetone. That these changes cannot be explained by dissociation has already been pointed out by Jones and Uhler, who suggest that they may be due to *solvation*. This is altogether reasonable, and the behavior of the spectrum is exactly what we should expect from the conclusions reached in the discussion of aqueous solutions. The red absorption then was ascribed to "simple" hydrates, such as contain 2 or 3 molecules of water or less. It is not unlikely that "simple" solvates of cobalt salts, in general, have this property of absorbing red light.

We should expect the power to form solvates to be greater for methyl alcohol than for ethyl alcohol, and greater for the latter than for acetone. Hence, in the case of ethyl alcohol and acetone at ordinary temperature, all the solvates formed are perhaps simple enough to exert powerful red absorption, while with methyl alcohol this is true only with concentrated solutions or at elevated temperatures. The differences in the structure of the band in the different solvents are, of course, to be expected, since the "absorbers" are different.

<div align="center">SALTS OF NICKEL.</div>

Among the more important investigations on the absorption spectra of nickel salts are the following:

Brewster,[1] in his early work on absorption, included the nitrate of nickel, and Emsmann[2] also studied the same salt.

Vogel[3] studied not only cobalt chloride but also the chloride of nickel, in connection with its power to absorb light.

[1] Phil. Mag. [4], **24**, 441 (1862).
[2] Pogg. Ann., Erganzb., **6**, 334 (1875).
[3] Ber. d. chem. Ges., **8**, 1533 (1875).

The work of Soret,[1] in 1878, also had to do with the chloride of nickel.

The splendid investigations of Hartley[2] on absorption spectra included also certain salts of nickel.

The work of Müller[3] in connection with salts of nickel calls for special comment. He tested Beer's law for certain salts of nickel and copper, and found that it holds for the sulphate and nitrate of nickel. The chloride and bromide of nickel showed deviations from the law. These deviations are to be explained, he thinks, on the basis of dissociation.

In a subsequent paper Müller[4] tests the above suggestion, and comes to the conclusion that dissociation alone cannot account for all the deviations from Beer's law. If the law does not hold, rise in temperature would produce a change in the absorption, and this would be similar to the effect produced by increase in concentration.

The fact is that rise in temperature produces effects on absorption different from those caused by increase in concentration, which shows that more than one factor must be taken into account in dealing with the causes of the deviation from Beer's law.

Müller thinks that both hydration and molecular complexes come into play.

It was thought neither necessary nor desirable to study the salts of nickel as exhaustively as those of cobalt. Several plates were, however, made, under the following conditions: Nickel chloride in water—Beer's law; nickel chloride in water—ions constant; nickel chloride in water—molecules constant; nickel chloride in water with calcium and aluminium chlorides; nickel sulphate in water—Beer's law; nickel acetate in water—Beer's law.

Only two of the nickel plates are given: Nickel chloride in water—Beer's law; and nickel chloride in water—molecules constant.

[1] Arch. Sci. Phys. Nat., **61,** 322 (1878).
[2] Trans. Roy. Dub. Soc. [2], **7,** 253 (1900); J. Chem. Soc., **83,** 221 (1903).
[3] Ann. Phys., **12,** 767 (1903).
[4] *Ibid.,* **21,** 515 (1906).
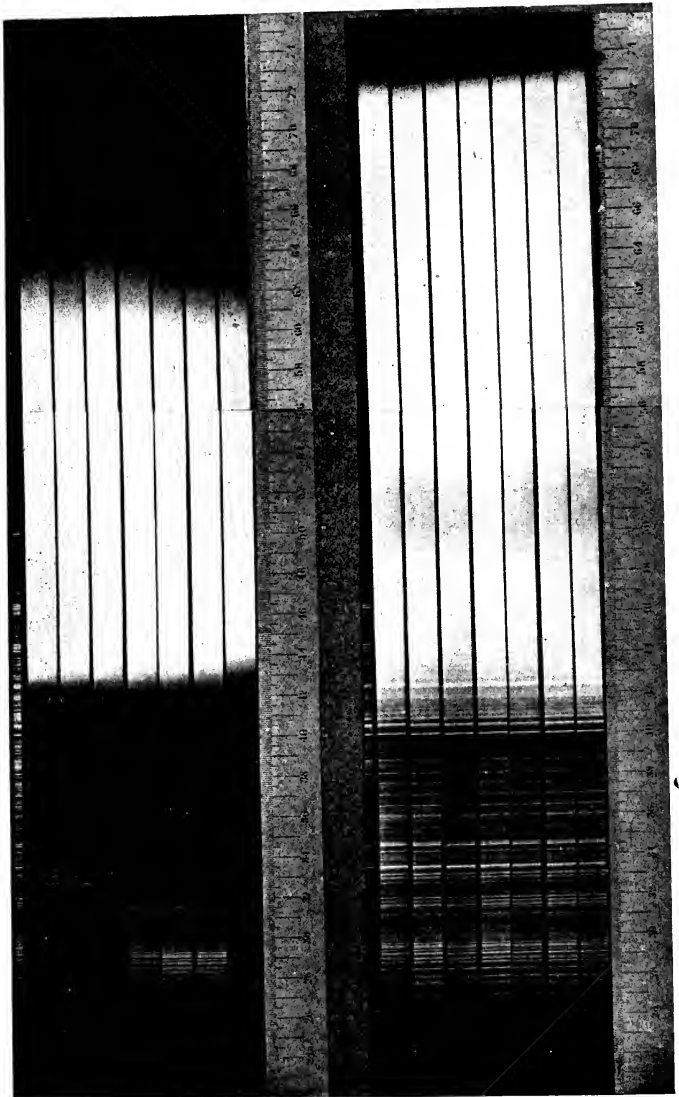
Plate IV.

A

B

Nickel Chloride in Water—Beer's Law (See Plate IV.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.66, 2.00, 1.33, 0.89, 0.61, 0.44, and 0.33, the corresponding depths of layer being 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.44, 0.33, 0.22, 0.15, 0.101, 0.073, and 0.055; the depth of layers were the same as for A.

The solutions were green, the more dilute ones tending towards a light yellowish-green. The exposures to the Nernst lamp and spark were $1^1/_6$ and 3 minutes, respectively, the slit having a width of 0.01 cm.

Plate IV., A, shows three regions of absorption, one in the extreme ultraviolet, a band in the end of the visible violet, and a band cutting off the extreme red. Besides this there is a rather strong general absorption in the entire ultraviolet beyond the absorption band in the end of the violet.

The extreme ultraviolet absorption perhaps narrows slightly with dilution, although from the second strip to the seventh the limit of transmission seems to remain almost fixed at λ 2550. The first solution, however, shows much more absorption in the whole ultraviolet region, including the band at λ 3960.

The band at λ 3960 narrows from the first to the third strips (counting from the scale) and then remains of constant width, the limits of transmission being approximately λ 3700 and λ 4230. The scale in the reproduction is shifted towards the red by nearly 50 A. U., due to the fact that in making the prints this was adjusted with reference to the narrow comparison strip seen at the top of the spectrogram. This strip is displaced, as may be seen by comparing the spark lines in the ultraviolet. The scale for the red end of the plate is, however, correctly placed, so that there is a slight discrepancy at the point where the two prints were joined together.

The absorption in the red shades off very gradually through a range of wave lengths of about 1000 A. U., being quite noticeable on the negative at λ 6100 in the strip corresponding to the most concentrated solution, and at λ 6200 in the strip

corresponding to the most dilute solution. The limits of transmission for the two strips are at λ 7150 and λ 7250, respectively. These measurements indicate a slight narrowing of the absorption band with dilution, but it must be remembered that photographic registration of the spectra is not the best method for studying such very hazy absorption bands, since a very slight change in the length of exposure or in the intensity of the source of light used may apparently shift the band very markedly. The only satisfactory method for studying such cases of hazy absorption is a spectrophotometric determination of the absorption coefficient for a number of wave lengths in the region.

In B the absorption in the extreme ultraviolet has disappeared, the last lines in the spark showing as well in the strips taken through the solutions as in the narrow comparison strip where there was nothing but air in the path of the beam of light.

The band at λ 3960 has become faint, but still shows distinctly on the negative. It remains unchanged in intensity in the seven strips on the spectrogram.

The absorption in the red, although present, as shown by the green color of the solutions in their bottles, was of too diffuse a character to be registered on the photographic plate, which, hence, shows complete transmission to beyond λ 7400. On the whole, except for the most concentrated solution, Beer's law seems to hold quite accurately for nickel chloride.

Nickel Chloride in Water—Molecules Constant (See Plate V.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.66, 2.18, 1.63, 1.22, 0.935, 0.750, and 0.610; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For set B the concentrations were 0.800, 0.660, 0.493, 0.365, 0.280, 0.220, and 0.160; the depths of the cell were the same as for set A. The exposures to the Nernst lamp and spark were 1 and 3 minutes, respectively, the slit having a width of 0.01 cm.

The general ultraviolet absorption beyond the λ 3960 band

Plate V.
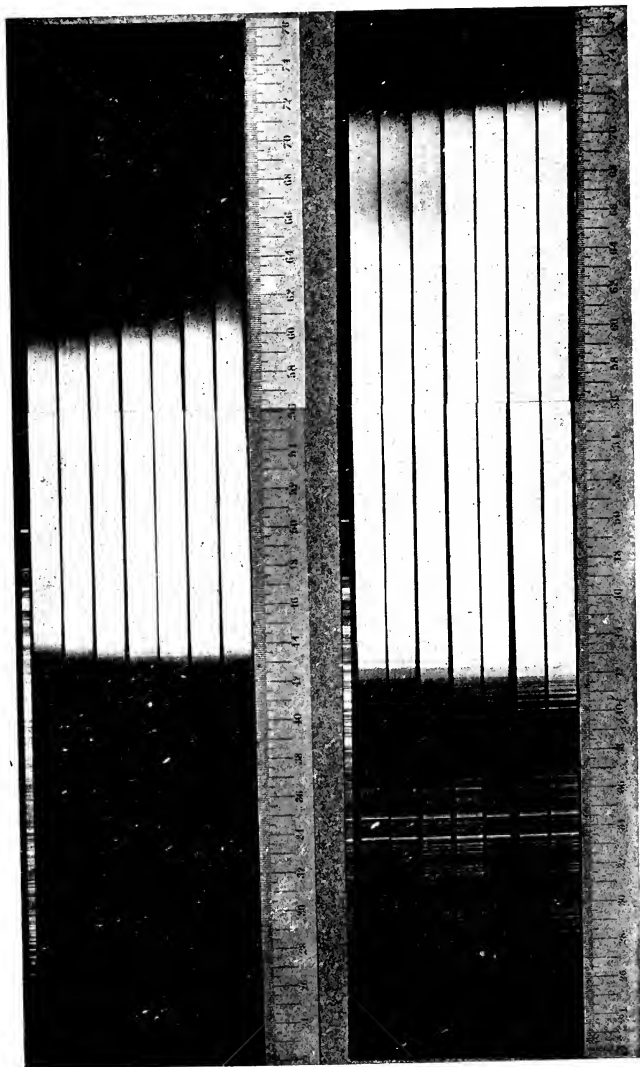
seems to remain nearly constant in the five most concentrated solutions of set A, then increases markedly in the sixth and seventh. The λ 3960 band narrows slightly from the first to the second strip (counting from the scale), then begins to widen, slowly at first, but more rapidly from the fifth to the seventh solutions.

In B the general ultraviolet absorption may still be seen, and it increases with dilution. The λ 3960 band also widens regularly with dilution. In the red the absorption increases regularly with dilution in both A and B.

The absorption bands of nickel salts seem to be very similar in their behavior to the green band of cobalt. In our study of that band we came to the conclusion that the power of absorption for green light is a property of the cobalt atom, and is only slightly affected by its immediate surroundings. Similarly, it appears from our study of nickel salts that the absorption shown by them is a property of the nickel atom, and there are only a few indications that it is changed very much by the immediate surroundings.

One of these is the marked widening of the λ 3960 band in nickel chloride as we approach a saturated solution. Others are the widening of the same band when large quantities of calcium or aluminium chlorides are added, and the appearance of the narrower bands in the orange and red, together with the change in the general absorption there under the same conditions. These point to the fact that the absorption of the simplest hydrates is somewhat different from that of the more complex ones, all of which (if there are several) seem to have about the same action on light. More definite conclusions on this subject must be deferred until the investigation shall have been extended to more compounds and under more varied conditions.

SALTS OF COPPER.

A number of investigators have included salts of copper among those whose absorption spectra they have studied. The results obtained with copper salts are, however, neither as interesting, nor apparently as important, as those furnished by cobalt, for example.

Hartley[1] included the chloride and bromide of copper in his elaborate investigations on absorption spectra; and Müller,[2] in his discussion of the deviations from Beer's law, dealt with the salts of both copper and nickel. Hartley explained the color changes in the case of copper chloride on addition of water as due to the formation of the compounds $CuCl_2.H_2O$ and $CuCl_2.2H_2O$ from the compound $CuCl_2$.

Donnan and Bassett,[3] in their interesting paper in which they develop the conception of complex ions as the cause of certain color changes in solution, also include cupric chloride.

Knoblauch[4] also studied the absorption spectra of copper sulphate.

A number of salts of copper were studied pretty thoroughly in the present connection. These include copper chloride in water—Beer's law; copper chloride in water—molecules constant; copper chloride in methyl alcohol—Beer's law; copper chloride in ethyl alcohol—Beer's law; copper chloride in acetone —Beer's law; copper chloride in methyl alcohol with water; copper chloride in ethyl alcohol with water; copper chloride in acetone with water; copper bromide in water—Beer's law; copper bromide in water—molecules constant; copper bromide in methyl alcohol—Beer's law; copper bromide in ethyl alcohol— Beer's law; copper bromide in methyl alcohol and water; copper bromide in ethyl alcohol and water; copper intrate in water— Beer's law; copper nitrate in water—molecules constant. Only three of the copper plates are given in this paper.

Copper Chloride in Water—Beer's Law (See Plate VI.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.5, 3.37, 2.25, 1.50, 1.038, 0.750, and 0.562; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.5, 1.12, 0.75, 0.50, 0.37, 0.25, and 0.19; the depths of cell were the same as in A. The concentrated solutions, as

[1] Trans. Roy. Dub. Soc. [2], **7**, 253 (1900).
[2] Ann. Phys., **12**, 767 (1903).
[3] J. Chem. Soc., **81**, 955 (1902).
[4] Wied Ann., **43**, 738 (1891).

Plate VI.
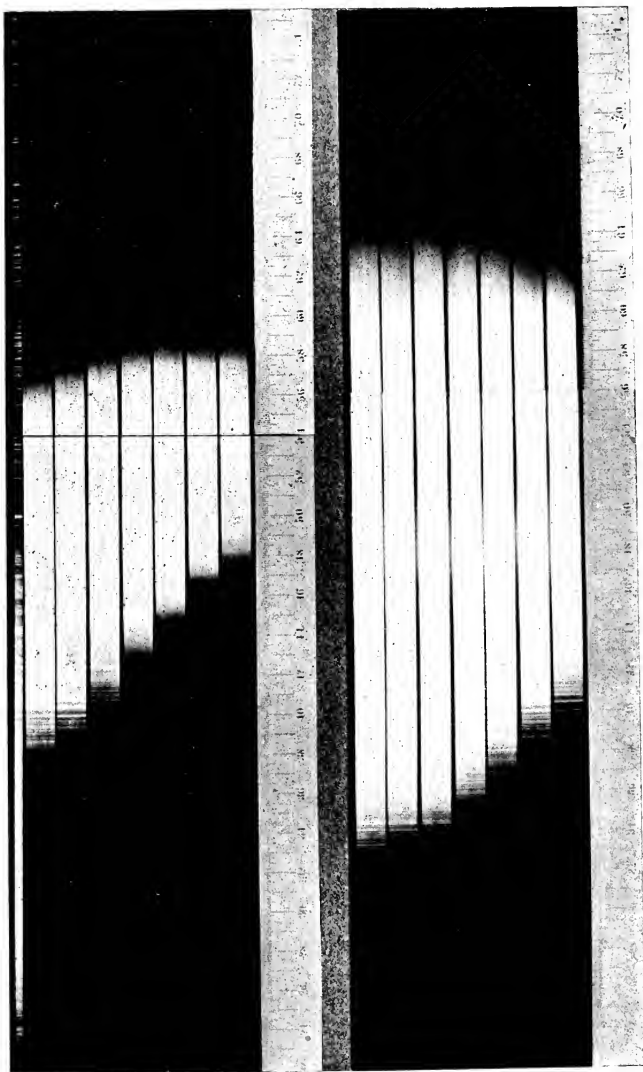
A

B

viewed in their bottles, were green. With dilution, the color changed through greenish-blue to a rather light blue. The exposures to the Nernst lamp and spark were $1\frac{1}{3}$ and 3 minutes, respectively, the slit having a width of 0.01 cm.

The spectrogram shows two regions of absorption, one in the blue, violet, and ultraviolet, and the other in the red. The two are evidently of quite different character, since the former narrows very rapidly with decrease in concentration, the other only slightly.

In A the first strip shows that transmission ends at λ 4750, while for the seventh strip the limit is at λ 3750. The change in absorption is most rapid from the second to the fifth strips, giving the edge of the band the form of a compound curve. In B the band narrows most rapidly from the first to the fourth strips, the corresponding limits of transmission being λ 3950 and λ 3400. In the seventh strip transmission ceases at λ 3250.

The edge of this ultraviolet band is fairly well-defined throughout, differing in this respect from that of the red band, which is somewhat hazy, although much less so than was the case with the red band of nickel.

In the red the first strip of A shows complete absorption from λ 5900 to the end of the spectrum. The seventh strip shows transmission as far as λ 6150. The corresponding readings for the first and seventh strips of B are λ 6450 and λ 6675. The edge is, however, very indefinitely defined in B, the shading being considerable.

It appears, therefore, that the red band also narrows with dilution, although much less than the ultraviolet one. It also narrows more rapidly at first, giving the edge of the band a curved form, concave towards shorter wave lengths. At great dilutions and correspondingly deep layers of solution, the edge of the band would in all probability be straight, and perpendicular to the length of the strips.

Copper Chloride in Water—Molecules Constant (See Plate VII.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.53, 3.59, 2.63, 1.97, 1.50,

1.19, and 0.97; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.50, 1.22, 0.91, 0.68, 0.52, 0.415, and 0.335; the depths of cell were the same as for A. The exposures to the light of the Nernst lamp and spark lasted 1½ and 3 minutes, respectively, the width of the slit being 0.01 cm.

In this spectrogram we find that the absorption band in the ultraviolet still narrows rapidly, while that in the red shows a tendency to widen with dilution. The limits of transmission shown by the first and seventh strips of A are λ 4750 and λ 4100, with the edge showing a compound curve similar to the one in Plate VI., A, but with less curvature. For the first and seventh strips of B the limits are λ 3990 and λ 3500, the edge forming a curved line convex towards the region of short wave lengths. In the red, the first strip of A gives the limit of transmission as λ 6050. In the second and third strip the limit is a little farther up in the red, being near λ 6075. In the fourth strip it is again at λ 6050, from which it moves gradually towards shorter wave lengths until the seventh strip is reached, where it is at λ 5975. The edge of the band is hence curved, with the convex side towards the longer wave lengths.

In B the band widens continuously with decreasing concentration, the limit of transmission for the solution corresponding to the first strip being λ 6500, while the seventh strip shows complete absorption at λ 6400. The edge is not sharply defined, the shading extending as far as λ 5000 with considerable intensity. From λ 6000 to λ 5950 the blackening of the negative increases very rapidly, and this position of most rapid increase in transmission seems to be sensibly the same for all the solutions of the one series. This is also nearly the position of the limit of transmission for the concentrated solutions used in A, and also in Plate VI., A. Hence, it seems likely that this is the real limit of the absorption band.

Copper Chloride in Methyl Alcohol—Beer's Law (See Plate VIII.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.744, 0.595, 0.469, 0.372,

Plate VII.
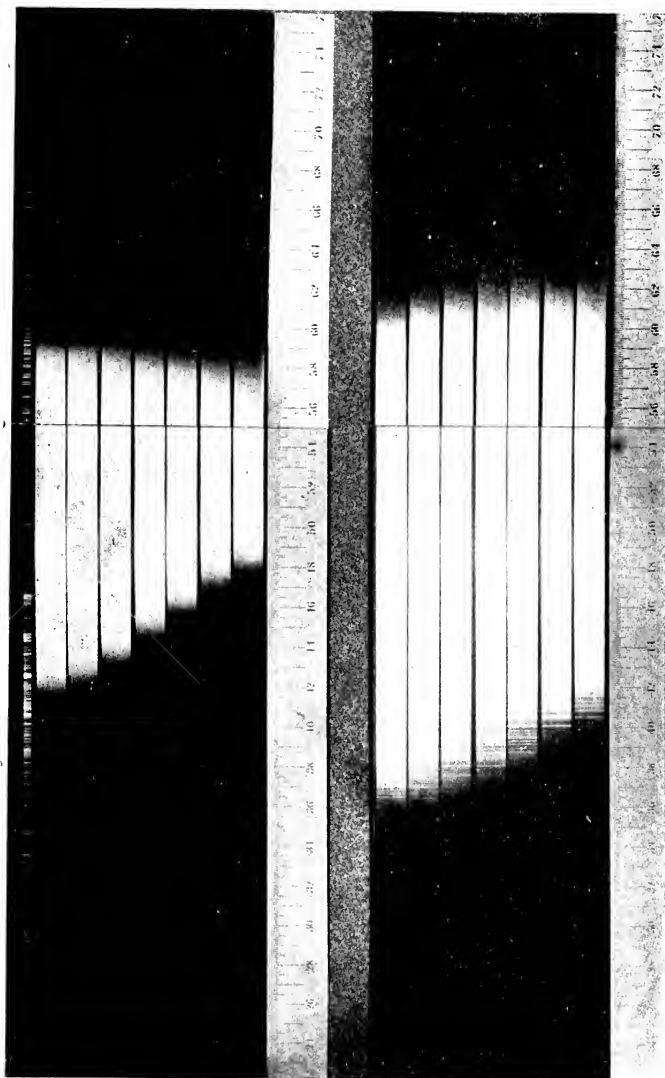
A

B

Plate VIII.

A

B
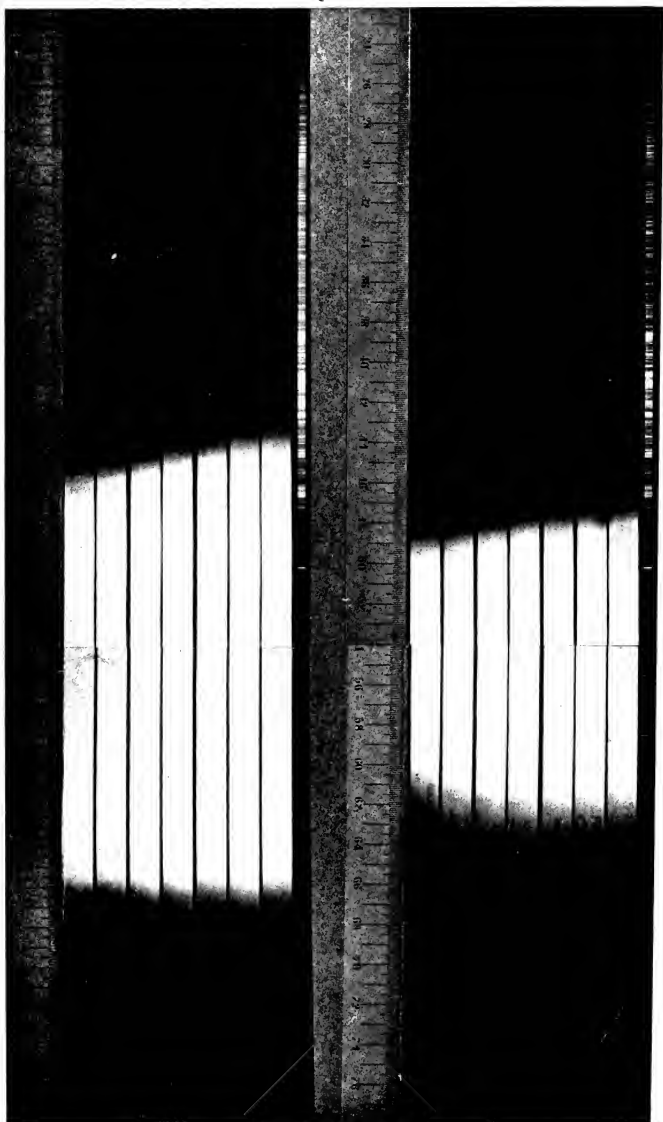
0.297, 0.233, and 0.186; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B the concentrations were 0.233, 0.186, 0.147, 0.116, 0.093, 0.073, and 0.058; the depths of absorbing layer were the same as in set A.

The solutions were all green, only the intensity of the color changing with dilution. Exposures to the light of the Nernst lamp and spark lasted for 1½ and 3 minutes, respectively, the slit having the usual width of 0.01 cm.

As in the aqueous solutions we have two regions of absorption, one in the blue, violet, and ultraviolet, the other in the red. Both regions contract somewhat when the concentration of the solutions is decreased, but the one in the violet region contracts much more than the one in the red.

The limit of transmission for the first strip in A is at λ 4800, while for the seventh strip it is at λ 4630. The edge of the band forms a line which is slightly curved at first, the concave side being towards the violet. From the third to the seventh strips the line formed by the edge is sensibly straight. In B the limit of transmission for the first strip is λ 4420, while for the seventh it is λ 4200, the edge forming a line which is very nearly straight. From the fourth to the seventh a slight curvature with the convex side towards the violet may be noted. On the whole, this band behaves exactly as it does in aqueous solution, the only difference being the greater deviation from Beer's law in the latter case.

In the red, the first strip in A shows transmission to λ 6500 with shading from λ 6050; the seventh strip, transmission to λ 6580, with shading from λ 6100. The first strip in B shows transmission to λ 6950, shading perceptibly from λ 6550, while the seventh strip shows transmission as far as λ 7020, with shading from λ 6600. In both sets, therefore, the band narrows slightly with dilution, and in B quite uniformly with the decrease of concentration. In A, however, the narrowing is considerably more rapid at first. Here, again, we find that the band behaves in a manner very similar to what we found in the aqueous solution, only the change is somewhat slower. The decrease in concentration from strip to strip here, however, is only about half what it was in the aqueous solution; and

taking this into consideration the difference is not as great as it seems at first glance.

In general, the absorption spectrum of copper salts in the region of the spectrum investigated is much simpler than that of cobalt salts, inasmuch as it presents only two, or at most three, absorption bands. Of these, only the one at λ 4730 in acetone solutions lies wholly in the spectral region studied; the band in the ultraviolet is what might be termed one-sided, no region of transparency on its more refrangible side having ever been found. The band in the red is, however, strictly a band, a region of transparency existing in the infra-red. The behavior of this band throughout strongly suggests the green band of cobalt salts in solution, while the ultraviolet absorption is somewhat different from anything we have found thus far, resembling more nearly the absorption of iron salts, to be discussed in the next section.

Since the absorption in the ultraviolet decreases rapidly with dilution, when the product of concentration and depth of layer is kept constant, it seems reasonable to suppose that the copper ion has little or nothing to do with it, and hence that it must be ascribed to the molecules; but as the absorption decreases with dilution, even when molecules are kept constant, without, however, entirely disappearing (as was the case with some cobalt bands), we must conclude that the absorbing power of a molecule is influenced considerably by its immediate surroundings. As usual, there are at least two possible ways of explaining the increase in the absorption with concentration when molecules are kept constant. One is to assume the formation of aggregates of molecules, and that the absorbing power of the molecule is increased thereby; the other is to assume the existence of solvates, and that the absorbing power of a molecule decreases with increase in the complexity of the solvate. To decide between these two possible explanations we need only take into account the change in the absorption produced by a rise in the temperature of the solution. This change is the same qualitatively as that produced by increasing the concentration. Molecular aggregates are broken down by rise in temperature, and hence, according to the assumption

made above as to the effect of aggregates on absorption, this should *decrease* the absorption instead of *increase* it. We must conclude, therefore, that the change in the absorption is not due to the formation of aggregates.

Solvates are made simpler both by increasing concentration and by rise in temperature, and, accordingly, from the assumption stated above regarding the effect of complexity of solvates on absorption, both changes should produce similar differences in the absorption spectrum. This is in accordance with observed facts. We conclude, therefore, that the ultraviolet absorption of solutions of copper salts is due to the "solvated" molecules of the dissolved salt, and that the absorbing power of such molecules is decreased as the complexity of the solvate increases.

It will be remembered that for equal concentrations the absorption in the region of shorter wave lengths is least in the aqueous solutions, then increases as we pass from methyl alcohol to ethyl alcohol. In general, also, it may be stated that the change in the absorption with dilution is greatest for the aqueous solution, and then decreases as we pass to methyl and ethyl alcohol. This is just what we should expect, since the power to form solvates is greater for water than for either of the alcohols, and greater for methyl than for ethyl alcohol; hence, in solutions of equal concentration the solvates should decrease in complexity when we pass in the direction—water, methyl alcohol, ethyl alcohol. Also the change in the complexity of the solvate, on dilution, should be greater in the water solutions than in the methyl or ethyl alcohol solutions.

The absorption band in the red narrows somewhat when the product of concentration and depth of absorbing layer is kept constant, but widens when molecules are kept constant. Its intensity does not change nearly as much as that of the violet band when the solvent is changed, the concentration being the chief factor which determines it. Hence we conclude that this band, like the green band of cobalt salts, is due to the metallic atom, and that its absorbing power is affected only slightly by its immediate surroundings. The peculiar behavior of the red band of copper chloride in methyl alcohol,

on addition of water, is interesting, especially as its explanation is not at all difficult, although it may not at first seem so simple. It will be recalled that here the band first widened when water was added, and then, as the amount of water was increased, it narrowed regularly. Now, when a small amount of water is added it is reasonable to conclude that the hydrates formed would be comparatively simple, and that as the amount of water is increased their complexity increases also.

We have stated that the effect of the surroundings on the absorption of the copper atom for this region of the spectrum is slight compared with what it is in the ultraviolet; but that it is quite appreciable is shown by the narrowing of the band wherever the conditions for Beer's law hold. We believe that this narrowing is due to a change in the complexity of the solvates. To explain the case in question, then, we need only say that the absorption of the comparatively simple hydrates formed when a small amount of water is added is greater than that of the methyl alcoholates already existing in the original solution; and that, therefore, the first effect observed is a widening of the band. Its subsequent narrowing as more water is added is, of course, due to the increase in the complexity of the hydrates.

In the similar solutions in ethyl alcohol the band narrowed from the very first, which is just what we should expect, since the solvates here are simpler than in methyl alcohol and hence their absorbing power would be equal to, or greater than, that of the simple hydrates first formed.

SALTS OF IRON.

A few salts of iron were studied under a few conditions. Thus: Ferric chloride in water—Beer's law; ferric chloride in water—molecules constant; ferric chloride with calcium chloride; ferric chloride with aluminium chloride; ferric chloride in methyl alcohol—Beer's law; ferric chloride in ethyl alcohol—Beer's law; ferric chloride in acetone—Beer's law. Only one iron plate is given, since the results obtained with salts of this metal are less interesting and less important than those with any other element.

Plate IX.

A

B

Ferric Chloride in Water—Beer's Law (See Plate IX.).

The concentrations of the solutions used in making the negative for A, Plate IX., beginning with the one whose spectrum is adjacent to the numbered scale, were 1.30, 0.97, 0.65, 0.43, 0.30, 0.22, and 0.16; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B, Plate IX., the concentrations were 0.22, 0.16, 0.11, 0.073, 0.051, 0.037, and 0.027; the depths of cell in both cases were the same as for A.

The most concentrated solutions, as viewed in their bottles, were reddish-orange, changing through orange-yellow to nearly colorless in the last members of the third series. The exposure to the light of the Nernst lamp lasted for 1 minute, the slit having a width of 0.01 cm. No exposure to the light from the spark was made, as it was ascertained by a preliminary trial that even the most dilute solution was opaque in the entire ultraviolet beyond λ 3600. A trial also showed complete transmission in the red as far as λ 7400, and hence no red-sensitive plates were used. Therefore, all the spectra of iron salts shown in this section seem to end at λ 6000 or near there, which simply shows that the Seed film used was not sensitive to light of longer wave length than about λ 6000.

The absorption decreases fairly regularly with dilution, the decrease being, however, less at high dilutions. The limits of transmission for the most concentrated and most dilute solutions of each of the three sets are λ 4850 to λ 4600, λ 4220 to λ 4100, and λ 3900 to λ 3800, respectively, the narrowing of the band in the first set amounting to 250 A. U., whereas, in the third set it was only 100 A. U.

An attempt was made to carry the dilution still farther, but it was found that the very dilute solutions changed color so rapidly with time that no confidence could be placed in the results obtained.

SALTS OF CHROMIUM.

A comparatively large number of investigators have worked on salts of chromium from the standpoint of absorption of light. We need only mention the work of Talbot,[1] Brewster,[2]

[1] Phil. Mag. [3], **4**, 112 (1834).
[2] Phil. Trans., **1835**, 1, 91; Phil. Mag. [4], **24**, 441 (1862).

Croft,[1] Müller,[2] Gladstone,[3] Melde,[4] the early work of Hartley,[5] Vierordt,[6] Vogel,[7] E. Wiedermann,[8] Soret,[9] Settegast,[10] Moissan,[11] Pulfrick,[12] Zimmermann,[13] Becquerel,[14] Liveing and Dewar,[15] Schunck,[16] Recoura,[17] and Sabatier.[18]

Knoblauch,[19] in his interesting and important investigation on the absorption spectra of very dilute solutions, studied a number of chromium compounds. These were the chloride, nitrate, sulphate, acetate, oxalate, potassium chrom-oxalate, and chrom-alum. Knoblauch directed a part of his work to testing the consequences of the then recently-proposed theory of electrolytic dissociation. According to this theory, the absorption spectrum of a concentrated solution must be different from that of a very dilute solution; and at dilutions of complete dissociation, all salts with colorless cations and a common colored anian, or salts with colorless anions and a colored cation must have the same absorption spectrum. Knoblauch found that neither of these conclusions from the theory were verified experimentally.

Ostwald[20] showed a little later that the second consequence of the theory is fully verified by experimental facts.

Knoblauch also tested Beer's law, and found that it held for many salts within wide limits of concentration. He concluded that the apparent deviations from the law are to be explained as due to chemical or physical changes in the solutions.

[1] Phil. Mag. [3], **21**, 197 (1842).
[2] Pogg. Ann., **72**, 76 (1847); **79**, 344 (1850).
[3] Phil. Mag. [4], **14**, 418 (1857); J. Chem. Soc., **10**, 79 (1858).
[4] Pogg. Ann., **124**, 91 (1865).
[5] P. Roy. Soc., **21**, 499 (1873).
[6] Ber. d. chem. Ges., **5**, 34 (1872).
[7] *Ibid.*, **11**, 913, 1363 (1878).
[8] Wied Ann., **5**, 500 (1878).
[9] Arch. Sci. Phys. Nat. [2], **61**, 322 (1878); [2], **63**, 89 (1878).
[10] Wied Ann., **7**, 244 (1879).
[11] Compt. rend., **93**, 1079 (1881).
[12] Z. Kryst., **6**, 142 (1882).
[13] Ann. Chem. (Liebig), **213**, 285 (1882).
[14] Ann. Chim. Phys. [5], **30**, 5 (1883).
[15] P. Roy. Soc., **35**, 71 (1883).
[16] Chem. News, **51**, 152 (1885).
[17] Compt. rend., **102**, 515 (1886); **112**, 1439 (1891).
[18] *Ibid.*, **103**, 49 (1886).
[19] Wied Ann., **43**, 738 (1891).
[20] Z. physik. Chem., **9**, 579 (1892).

Hartley,[1] in his elaborate investigations on absorption spectra, studied a number of salts of chromium. The salt $Cr(NO_3)_3.9H_2O$ is violet in color. When heated to 100° it changes to green. Hartley concludes that the violet are the normal salts of chromium, while the green are chromyl salts, thus:

	Violet salts.	Green salts.
Chloride	$CrCl_3.3H_2O$	$Cr_2OCl_4.2H_2O$
Sulphate	$Cr_2(SO_4)_3.15H_2O$	$Cr_2O(SO_4)_2.xH_2O$
Nitrate	$Cr_2(NO_3)_6.9H_2O$	$Cr_2O(NO_3)_4.H_2O$

An interesting paper by Vernon[2] on "The Dissociation of Electrolytes in Solution as Shown by Colorimetric Determinations" was published in sections in the *Chemical News*. Chromium plays in this work what might be termed the exceptional rôle, as is seen from the following conclusions drawn by the author:[3]

"Almost all the solutions of the thirty-five colored salts examined show considerable decrease in color effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the color of whose solutions on gradual dilution either remains constant or increases slightly. All solutions of salts, with the exception of those of certain chromium derivatives and perhaps of potassium permanganate, increase considerably in color effect on being heated."

Lapraik[4] has described a large number of empirical relations between the absorption spectra of compounds of chromium. Certain classes of chromium compounds were found to have the same absorption spectra in solution and in the solid state. The band λ 710 to λ 692 is present in all of the chromium compounds investigated, with the exception of potassium chromium cyanide. In certain compounds, however, the band is displaced somewhat from the above position.

The broad absorption in the green in the region of λ 550 to λ 650 is present in all chromium compounds, sometimes dis-

[1] Chem. News, **65**, 15 (1892); Trans. Roy. Soc. Dublin [2], **7**, 253 (1900).
[2] Chem. News, **66**, 104, 114, 141, and 152 (1892).
[3] *Ibid.*, **66**, 154 (1892).
[4] J. prakt. Chem., **47**, 305 (1893).

placed somewhat towards the red, in other compounds towards the blue, as referred to the above wave lengths.

Etard[1] studied the sulphate of chromium, chrome-alum, and violet chromium nitrate. He found a band in the red, which was characteristic of chromium salts, and which extended from 670 to 678. He concluded that the absorption spectra of chromium salts are due to the molecules.

The absorption bands produced by an element are displaced in position, or may cease to exist entirely, depending upon the nature of the whole molecule which is in solution, *i. e.*, upon the particular compound of the element studied.

Two salts of chromium have been brought within the scope of this investigation, and under the following conditions: Chromium chloride in water—Beer's law; chromium chloride in water—molecules constant; chromium chloride with calcium chloride and aluminium chloride; chromium nitrate in water— Beer's law; chromium nitrate in water—molecules constant.

Only one chromium plate is given.

Chromium Chloride in Water—Beer's Law.   (See Plate X., A.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.53, 0.40, 0.26, 0.17, 0.12, 0.09, and 0.07; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm.

The exposures to the light of the Nernst lamp and spark lasted $1\frac{1}{6}$ minutes and 3 minutes respectively, the slit having a width of 0.01 cm.

In deep layers the more concentrated solutions were red, while in shallow layers they were green. The dilute solutions, as seen in their bottles, appeared green.

The spectrogram shows three regions of absorption: One is located in the extreme ultraviolet, cutting off the part of the spectrum lying to the more refrangible side of λ 2840. Another absorption band is in the violet, its more refrangible limit being at λ 3900, and moderately well-defined, while the red edge, which is more hazy, is near λ 4450. A third band is located

[1] Compt. rend., **120**, 1057 (1895).

Plate X.

A

B
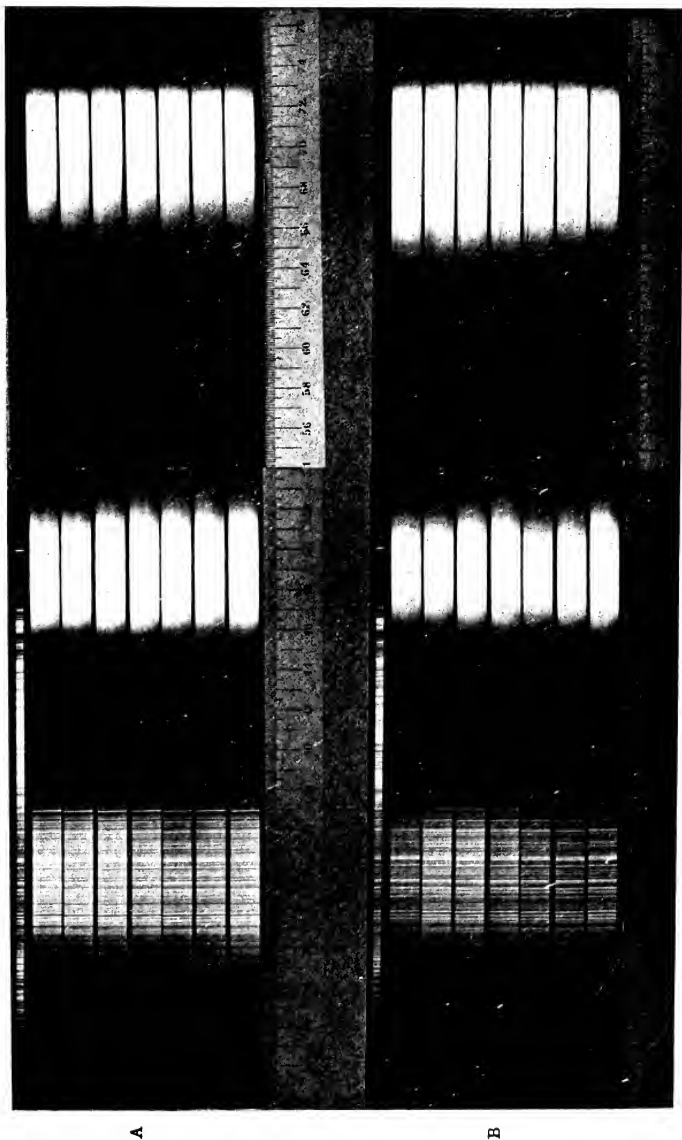
in the yellow and orange. Both edges of this band are very diffuse, the red edge slightly more than the blue. The spectrograms indicate that the opposite is the case, but this is due to the fact that the blue edge of the band falls near the region or minimum sensibility of the Seed film, and, hence, the shading there is very much accentuated. The limits of transmission are at λ 5650 and about λ 6200, although there is considerable absorption as far "down" as λ 5200 and as far up as λ 6750. From λ 6800 to the end of the visible red the solutions are remarkably transparent. This was made very evident by the fact that a concentrated solution, about 20 cm. in depth, still transmitted red light freely, although not a trace of green could be seen through a layer 5 cm. deep.

The width of all these bands is absolutely unchanged by change in dilution, within the limits of concentration here used; hence the absorption is strictly proportional to the number of chromium atoms in the path of the beam of light, whether they exist as ions or combined with other atoms in a molecule.

Chromium Chloride in Water—Molecules Constant (See Plate X., B.).

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.45, 0.35, 0.245, 0.173, 0.125, 0.093, and 0.074; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. The exposures to the light of the Nernst lamp and spark lasted, $1\frac{1}{6}$ and 3 minutes, respectively; the width of the slit was 0.01 cm.

The spectrogram shows the same regions of absorption as A, but in this case they all widen with decrease in concentration, as was to be expected. The bands all widen to nearly the same extent. The shading on the red side of the least refrangible band does not extend any farther into the red with decrease in concentration, this band having, therefore, a rather well-defined limit near λ 6800.

A rather narrow band of absorption may be seen at λ 6690.

It is faint and scarcely noticeable in A. Its width is not easily determined, but appears to be only about 30 A. U.

[*The remainder of this paper will appear in the April number of This Journal.*]

THE ELECTROMOTIVE FORCE OF NICKEL AND THE EFFECT OF OCCLUDED HYDROGEN.[1]

By E. P. Schoch.

The published accounts concerning the electromotive force of nickel are not only vague, but in the main conflicting. Neumann (1),[2] Siemens (2), and Euler (3) locate the potential of nickel in the neighborhood of 0.50 volt.[3] Other investigators (4) have not been able to satisfactorily duplicate this or any other value for the potential. More recently Muthmann and Fraunberger (5) placed the value of the potential Ni–N/1 NiSO$_4$ at 0.88 volt. They considered that the potential of "active" nickel is obtained only when passivizing influences are completely excluded. Hence they polarized nickel extensively with hydrogen in distilled water, then quickly transferred it to a N/1 nickel sulphate solution and observed the potential. In text-books (9) this high value has displaced the older determination of Neumann. However, the well-known fact that nickel occludes hydrogen, coupled with the results of Richards and Behr (10) on the effect of occluded hydrogen,[4] lead me to suspect that this high value is due, in part at least, to occluded hydrogen, and that it does not represent the reversible potential; and the following preliminary experiments showed me where the reversible potential is probably located.

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[1] This and the following paper deal primarily with sulphate electrolytes.

[2] The numbers in parentheses refer to references given at the end of this paper.

[3] The potentials given in this paper are expressed in international volts. They refer to the normal calomel electrode as an arbitrary zero, and the values given are the observed values without any corrections. The measurements are made by the well-known Poggendorff compensation method with a capillary electrometer as a zero instrument.

[4] Richards and Behr located the potential of iron in N/1 ferrous sulphate solution at 0.71 volt, and showed that occluded hydrogen may produce much higher potentials. Muthmann and Fraunberger's value, obtained with iron polarized in distilled water and then transferred to N/1 ferrous sulphate solution, is 0.94 volt.

Nickel poles may show widely different potentials, depending upon their preparation, previous exposure, etc. Thus, nickel that has been lying in air will show in $N/1$ nickel sulphate solutions potentials ranging from 0.25 to 0.32 volt. Poles that have been prepared by boiling in sodium hydroxide solution and then dipping in concentrated hydrochloric acid showed 0.875 volt in the same electrolyte ($N/1$ nickel sulphate solution). Polarized anodically or cathodically in any liquid and then transferred to $N/1$ nickel sulphate solution, nickel poles will show almost any potential between 0.88 and zero or even lower. However, when nickel is allowed to remain in nickel sulphate solution free from air it attains a potential between 0.43 and 0.50 volt, irrespective of the potential which it showed just before. In $N/1$ sulphuric acid and in dilute hydrochloric acid, in both of which it dissolves slowly, nickel gives a potential of approximately 0.40 volt. At temperatures from 70° to 100° C., the metal attains approximately the same potential as at ordinary temperatures. At high temperatures nickel will attain this final potential very rapidly, while at ordinary temperatures more time is required.

These experiments indicate that the reversible potential of nickel is between 0.45 and 0.50 volt. A more accurate location of this potential is presented in the following pages.

The Potential of Nickel.

Since the lower potentials may be produced by air, it is necessary to remove and exclude this entirely, and for this purpose the liquids with the poles in them were boiled vigorously for several minutes and then cooled without allowing air to get into the apparatus, which was made as follows: A Bohemian flask, preferably one with a short, wide neck, is closed with a rubber stopper, through which is fitted the stem of the nickel pole and a glass syphon. The latter should terminate just at the lower surface of the stopper; the other end dips into another flask. The two flasks are clamped on a suitable stand; the stoppered flask is filled half full with the electrolyte and into the other flask is poured somewhat more of the electrolyte than would fill the first flask and the

tube, so that enough liquid will remain in the second flask to serve as a seal. The liquid in both flasks is boiled vigorously for several minutes. When the heat is withdrawn the condensation of the steam in the first flask will draw the liquid over from the second flask. In order to avoid a drawing over of solution saturated with air, which would occur if the large volume of liquid in the first flask were allowed to cool slowly, the stoppered flask is cooled rapidly by means of ice water. If the pole is to be kept for any length of time, mercury is poured into a second flask so as to serve as a seal to the glass tube.

The results indicate that oxygen or air may thus be almost completely removed. Any remaining portion of it will be so small as to lower the potential only 5 to 10 millivolts. Hydrogen cannot be removed nearly as completely; after boiling it may still be present in sufficient amount to raise the potential as much as 50 millivolts.[1]

The question of the neutrality of the solution had to be considered carefully. Not only do acidified solutions give a lower potential, but the merest trace of acidity is particularly effective. Thus, two samples of well-crystallized nickel sulphate (Merck) taken from the same lot gave potentials differing by 50 millivolts. The one which produced the lower potential was faintly acid to litmus; the other was neutral. I neutralized the remaining acidity of the first one with a slight excess of sodium hydroxide, filtered off the small amount of precipitate formed, and found that this liquid gave the same potential as the other neutral sample above. By this means I could get more closely agreeing results than I could without it, and since this was a step towards securing readily reproducible conditions, I have treated in the same way all solutions which are referred to as *neutral*.

The following results were obtained with neutral $N/1$ nickel sulphate solution, at ordinary temperatures (26° C.):

1. Commercial sheet nickel, 12–36 hours after preparation of pole, 0.47 volt.

[1] The effect of hydrogen, which raises the potential, is shown farther on in this paper, and that of oxygen, which lowers the potential, is discussed in the following paper on "The Behavior of the Nickel Anode."

2. Electrolytic nickel, Kahlbaum's, 12–36 hours after preparation of pole, 0.465 volt.

3. Electrolytic nickel, my own preparation, 12–36 hours after preparation of pole, 0.47 volt.

Nos. 1 and 3, after standing for six weeks, during which time the syphon was closed with a mercury seal, showed 0.48 volt, while another pole of commercial sheet nickel, after nine weeks, showed 0.487 volt.

Since the results obtained with commercial sheet nickel agree with those obtained with electrolytic nickel, only sheet nickel was used in the remaining experiments.[1]

A sample of commercial nickel was polarized cathodically and was then put into the flask, boiled, and cooled. It showed a potential of 0.55. After standing for six weeks it showed a potential of 0.485.

A nickel wire, No. 18 B & S gauge, was bent in the form of a spiral similar to the carbon filament in some of the electric lights. The ends were connected by clamps to two stout copper wires, which passed through the rubber stopper in a 500 cc. flask. This stopper was also fitted with two glass tubes by means of which the air in the flask was completely displaced by pure nitrogen. The nickel wire was heated to white heat in this gas. After allowing the flask to stand and cool, nickel sulphate solution which had been boiled and cooled under an atmosphere of nitrogen was introduced. Of course, only the nickel was allowed to dip into the electrolyte. This pole gave the following results:

At first, volt.	After 12 hrs., volt.	After 24 hrs., volt.	After 36 hrs., volt.
0.49	0.48	0.48	0.46

Since the solubility of the nickel anode is largely increased by hydrogen and halide ions, it is desirable to know if these ions affect the maximum electromotive force of nickel.

The potential of $Ni–N/1$ $NiCl_2$ at ordinary temperatures (26° C.) was found to be 0.42 volt—a result that may be con-

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[1] The possibility that the potential may be due wholly or in part to a slight quantity of impurities in the metal is excluded by the fact that after extensive electrolytic corrosion the nickel shows the same potential as before. This was observed repeatedly in connection with the study of the behavior of the nickel anode.

sidered to be in accord with the potential of Ni-N/1 NiSO₄. Hence the potentials of nickel in nickel sulphate solutions which have only a relatively small amount of halide ions in them should not differ essentially from the potential obtained when the latter are absent.

I obtained the following results:

(1) An electrolyte 1/10 normal with potassium chloride, and 9/10 normal with nickel sulphate showed at first 0.46 volt; after 24 hours, 0.475 volt; after 36 hours, 0.475 volt.

(2) An electrolyte 1/10 normal with potassium fluoride and 9/10 normal with nickel sulphate showed, after 12 hours, 0.475 volt.

The effect of acidification was ascertained, with the following results:

1. An electrolyte 1/2500 normal with sulphuric acid and normal with nickel sulphate showed, for 12 hours, 0.455 volt.

2. An electrolyte which was 1/10 normal with sulphuric acid and normal with nickel sulphate showed, for 12 hours, 0.42 volt.

It is notable that neither halide nor hydrogen ions raise the potential. An explanation of the action of the acid in producing lower potentials is given on page 219.

The effect of increase in temperature appears to be to lower the potential. A nickel pole in neutral N/1 nickel sulphate solution which showed 0.47 volt at 26° gave in one case 0.42 volt at 95° C.; in other cases, 0.434 and 0.44 volt, respectively. A value higher than 0.44 volt was never observed.

The effect of concentration is most strikingly shown by using for an electrolyte a solution containing no nickel. Potassium or sodium sulphate serve equally well, provided they are both absolutely neutral. Normal potassium sulphate gave, after 12 hours, 0.56 volt at 26°. Since very dilute nickel sulphate appears to introduce difficulties into the measurement, I decided to use nickel sulphate with potassium sulphate in such concentrations that the sum of the normalities was always the same. I obtained the following results:

1. An electrolyte which is 1/100 normal with nickel sulphate and 99/100 normal with potassium sulphate gave, at

first, 0.53 volt, and, after 24 hours, 0.54 volt, where it remained constant for the next 24 hours.

2. An electrolyte which is 1/10 normal with nickel sulphate and 9/10 normal with potassium sulphate gave, at first, 0.50 volt, and, after 12 hours, 0.51 volt, where it remained constant.

It should be mentioned in this connection that there are indications of a reaction between nickel and potassium sulphate solution as a result of which a nickel-potassium alloy may be formed.[1] However, this appears to have no particular effect upon the potential, because nickel thus affected gives the usual potential in N/1 nickel sulphate solution.

Although the potassium sulphate employed in the foregoing experiments was strictly neutral to litmus, yet the question may be raised: Is the higher potential perhaps due to a lesser concentration of hydrogen ions in N/1 potassium sulphate than in N/1 nickel sulphate solution? Hence the following experiments were carried out:

1. Normal potassium sulphate which was also 1/2500 normal with potassium hydroxide gave:

At first, volt.	After 12 hrs., volt.	After 24 hrs., volt.	After 36 hrs., volt.
0.50	0.51	0.54	0.533

2. Normal potassium sulphate which was also 1/250 normal with potassium hydroxide gave, after 12 hours, 0.52 volt.

3. N/10 potassium hydroxide gave, after 12 hours, 0.52 volt.

4. N/1 potassium sulphate with N/2500 sulphuric acid showed, after 12 hours, 0.537 volt.

These results prove that the higher potentials shown by nickel in potassium sulphate solutions cannot be due to greater alkalinity or acidity of the solutions, because *both* lower the potential. Altogether we may safely conclude that the higher potentials are due to the difference in the concentrations of the nickel ions, and thus we have secured one of the most reliable indications of a reversible potential.

From the preceding data I have selected the value 0.48

[1] See page 244 of the following paper on "The Behavior of the Nickel Anode."

volt for the potential Ni–N/1 $NiSO_4$. This may be considered to be correct to within ±5 millivolts. A nickel pole, which within 12 hours will approach this value—being at most 5 to 10 millivolts too low—can be prepared by using commercial nickel, or electrolytic nickel which has been exposed to the air long enough to allow all the hydrogen to escape. The electrolyte should be absolutely neutral to litmus and the pole should be prepared by boiling and cooling, as above directed.

Finally, I wish to point out why earlier determinations resulted in different values for the electromotive force of nickel. Neumann (1) prepared his nickel pole by electrolysis; hence his nickel contained hydrogen and gave too high a potential. Siemens (2) resorted to alternate cathodic and anodic polarization, and finally prepared some nickel by electrolytic deposition, with special precautions as to possible contamination from anodic products. But none of his directions are of any essential benefit—in fact, anodic and cathodic polarization are objectionable. Euler (3) directs that samples of nickel be kept in nickel sulphate solution from 6 to 8 days, and he advises the expulsion and exclusion of the air from the electrolyte, but he does not urge the latter, and he says nothing special about acidity. He obtained with three different samples of nickel the value Ni–N/1 $NiSO_4$ = 0.466 volt. This accords with my own results when the slight differences in procedure are allowed for.

The Effect of Occluded Hydrogen.

Raoult (14) found that a piece of very porous nickel, after polarization in water, evolved 165 volumes of hydrogen when allowed to remain in water for two or three days afterward. He found that there is considerable difference in the amount of hydrogen occluded by different samples of nickel, less porous samples occluding very little. Thoma and others (16) also observed that nickel, on polarization, absorbs hydrogen. It is commonly considered that the "curling up" of electrolytically deposited nickel plate is due to the codeposited hydrogen (17). If the nickel has been deposited very rapidly a

greater amount of hydrogen is enclosed; the uneven escape of this produces a strain in the plate and the latter cracks and peels off. Any agencies which lessen the amount of enclosed hydrogen (such as small current densities or higher temperature)(18) tend to prevent this trouble.[1]

None of these experimenters have studied the effect of hydrogen upon the potential of nickel. Hence my first effort was directed to ascertain this. I took good commercial sheet nickel which had been lying exposed to the air, and placed it in a wide test tube in such a way that a narrow strip or "lip" of sheet nickel extended through a slit in the rubber stopper which closed the test tube. Two glass tubes also passed through the stopper: one, which extended just through the stopper, was bent in the shape of a syphon; the other tube extended to the bottom of the test tube. The test tube was filled with $N/1$ nickel sulphate solution and closed with the rubber stopper, so that all the air was excluded. By means of the liquid in the syphon tube and of the "lip" of sheet nickel, electrical contact was made. The potential of the nickel at first was 0.30 volt. It rose steadily until after three days it was 0.470 volt, and remained there for two days. Hydrogen gas, prepared by electrolysis with nickel poles in sodium hydroxide solution and filtered through a cotton plug, was now passed through the solution by means of the tube which reached to the bottom of the test tube. The potential rose to 0.62 volt almost immediately. The test tube and contents were now heated to boiling to expel the hydrogen as much as possible. The apparatus was so arranged that on cooling nothing but boiled nickel sulphate solution was drawn into the test tube. At ordinary temperatures the nickel then showed a potential of 0.50 volt. Very little change in this potential was observed during two days. Then the apparatus was completely shut off from contact with air by dipping the end of the syphon tube into mercury, and thus it was allowed to stand for three weeks. After this time the potential of the nickel was 0.48 volt. On

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[1] The results of Baxter (20), Sieverts (26), and others on the absorption of hydrogen by nickel at high temperatures have probably no direct connection with the results obtainable at ordinary temperatures.

repeating the experiment I obtained the same results, except that the hydrogen caused a rise of potential to 0.605 volt only.

It is evident that occluded hydrogen raises the potential of solid nickel. The next question of interest is: What is the potential of finely divided *porous* nickel (reduced by hydrogen at a low temperature), and has hydrogen the same effect upon it? The question, as applied to iron, has been answered with great care by Richards and Behr (10), and hence the results for nickel become doubly important, because, through comparison, a check can be made on the potential of nickel.

Pure nickel nitrate (Kahlbaum's)—free from cobalt—was subjected to two fractional crystallizations, and was then dried and ignited in a platinum dish. The resulting nickel oxide was reduced by a current of hydrogen in an ordinary combustion furnace. The hydrogen was prepared from zinc and sulphuric acid and conducted through acidified potassium permanganate solution, then over dry sodium hydroxide, and finally filtered through a bit of cotton. The sample of nickel thus reduced was allowed to cool in hydrogen and was then transferred to a little cup made as follows: Into the bottom of the "cup" of a "thistle top" funnel was fused a piece of platinum wire in such a way that a short portion of it extended into the cup and the other into the stem below, which was completely closed by fusion just below the cup, and was bent up until it touched the cup. The nickel was well tapped into this cup so that none of the platinum wire was exposed. The stem of the funnel was passed through one hole of a rubber stopper which fitted into a 500 cc. flask. Through the stopper also passed two other glass tubes, one of which extended to the bottom of the flask and the other ended just below the stopper. By means of these two tubes a current of gas or liquid could be introduced into the flask. The flask was filled with hydrogen gas and then N/1 nickel sulphate solution, which had been previously boiled and cooled in an atmosphere of hydrogen, was admitted. Electrical connection with the nickel was made by

means of mercury poured into the stem of the cup, and the calomel electrode was connected through the liquid in one of the glass connecting tubes. Under these conditions the nickel showed the following potentials:

At first, volt.	After 12 hrs., volt.	After 24 hrs., volt.	After 36 hrs., volt.
0.56	0.59	0.60	0.59

The flask and contents were now heated until the liquid boiled and all hydrogen gas was expelled. The conducting tubes on the outside were connected with the second flask in which nickel sulphate solution was boiled so that when the steam in the closed flask condensed, the solution from the second flask was drawn over, completely filling the first flask. After the flask and contents had cooled thoroughly, the nickel showed a potential of 0.535 volt, which it held steadily for 24 hours. The second sample of nickel was prepared just in the same way as the first, but after the reduction was complete the hydrogen was displaced by a current of pure nitrogen obtained from air by treatment with a large excess of alkaline pyrogallate solution. The flames were then turned out and the nickel allowed to cool in this atmosphere. This nickel was introduced into the cup as above, and the flask filled with nitrogen gas. This was displaced by nickel sulphate solution which had been boiled and then cooled in an atmosphere of nitrogen. This nickel gave a potential of 0.522 volt, which it maintained for 24 hours. After two months its potential was 0.518 volt, while a piece of commercial sheet nickel in the same apparatus with it showed 0.487 volt. It appears from this that the potential of finely divided porous nickel is about 0.52 volt, or about 0.04 volt greater than the potential of solid nickel. Richards and Behr found the potential of porous iron to be 0.03 volt greater than that of solid iron (0.71 volt). The nickel that has been cooled in hydrogen shows a considerably (0.07 volt) greater potential. Heating the nickel in the boiling electrolyte evidently removed most of the hydrogen, but a small amount remained and was removed only by slow diffusion. In this respect the spongy nickel behaved like solid nickel. Richards and Behr also

found it very difficult to remove the last traces of hydrogen from iron.

I proceeded next to ascertain the effect of hydrogen produced in the nickel by cathodic polarization.

A nickel cathode polarized in an acid may show, while polarized, any potential from 0.50 volt upward to 1.00 volt and over. When the current is cut off, the polarization potential sinks more or less rapidly until it arrives in the neighborhood of 0.50, where it appears to stop. With samples of nickel which do not appear to be porous the drop takes place very rapidly, while with porous samples, several days may be required.[1] The maximum of polarization can be observed only while the polarizing current is turned on. Of course, this measurement can be made only by some means which will avoid the introduction of the drop in voltage due to resistance within the electrolyte. This object is usually attained by connecting the calomel electrode through a tube drawn to a fine capillary, the end of which is bent so that the opening may be applied right against the electrode. Mechanical means for disconnecting the electrolyzing current and quickly connecting the auxiliary electrode do not give the maximum polarization values, but give an irregularly lower value. As is well known, these are all characteristics of hydrogen polarization on such metals as platinum, gold, mercury, etc.

When the polarized cathodes are quickly transferred to N/1 nickel sulphate solution they show a higher potential than they showed just before being transferred and while they were in the acid. This is what we would expect, for the concentration of the hydrogen ions in the neutral nickel sulphate solution is much smaller than in the acid. Such trials can be made only when the poles have arrived at the point where the drop in potential is very slow, and even then they can be made successfully only with samples with which the drop in potential is altogether slow—that is, with samples

[1] A porous surface may be readily obtained by means of electrolytic deposition with a relatively large current, alternating short periods of deposition with longer periods of rest.

which are comparatively porous, or in which the occluded hydrogen has penetrated to a considerable depth. Muthmann and Fraunberger prepared such a sample by long polarization in pure water. By this means, these experimenters obtained 0.88 volt as the maximum value. The highest value I obtained by this method is 0.84 volt. But I attach no special significance to obtaining any particular one of these values because it seems to me to be only a question of how rapidly the metal is transferred, how porous it is, etc. (see page 230).

When nickel has been allowed to remain in hydrochloric or dilute sulphuric acid for some time it will show a potential of about 0.40 volt. If it is then well rinsed with distilled water and dipped into N/1 nickel sulphate solution, it will show a potential of 0.50 to 0.65 volt and more. However, if the solution is then made faintly acid, the potential will fall, and with stronger acidification, the potential shown will be 0.45 or even 0.40 volt. This effect of acidification was also observed by Muthmann and Fraunberger. It is readily understood when we recall that nickel can displace hydrogen from acids. Although the hydrogen in the deeper recesses may be very concentrated as a result of the action of the capillary forces, that of the outer layers, which shuts out the electrolyte from the deeper recesses, cannot be concentrated beyond the point at which its solution tension is equal to that of the nickel, and since this "surface" hydrogen is constantly suffering a loss through diffusion the potential exhibited will be *less* than that of the nickel.[1] The drop in potential observed when a nickel sulphate solution is acidified is the result of the same conditions just described. On account of this observation, Muthmann and Fraunberger ascribed to

[1] It might be objected that the potential of nickel in contact with an electrolyte containing none of its ions should be greater than that which it shows when in contact with N/1 nickel sulphate solution. However, it is a matter of common experience with other metals, copper, zinc, etc., that no such great difference exists, and the explanation is that the layer of liquid on the surface of the metal is almost immediately changed to a solution of a salt of the metal. Still it may be objected that if the potential due to the nickel is greater than that due to the hydrogen, the potential due to the nickel should be the one observed. This would be the case if nickel did not possess an extremely small velocity of solution. The loss of hydrogen by diffusion probably takes place comparatively rapidly and the nickel keeps up the supply by reaction; this, together with a small solution velocity, prevents the nickel from exerting its maximum solution pressure.

sulphuric acid a passivizing influence, but in the light of the facts to be presented later, acids are shown to be *activizing* and not passivizing agents. The discrepancy in the interpretation is due to the difference in the location of the equilibrium potential of nickel.

The following procedure enabled me to get the greatest occlusion of hydrogen and hence the highest potential. A piece of sheet nickel was boiled in concentrated sodium hydroxide solution for 15–30 minutes,[1] and then placed in concentrated hydrochloric acid for the same length of time. It was then rinsed with water and placed in N/1 nickel sulphate solution which had been boiled (to remove the air) and cooled. This sample showed a potential of 0.875 volt for five days afterwards. A striking behavior of this electrode showed itself when it was again used as a cathode. Before the current was turned on it showed the high value just above mentioned, but as soon as a current of very low density was turned on, the potential dropped to about 0.50, rising from this on with the current density. A day or two after the current was cut off, the electrode exhibited the former high potential. This behavior is characteristic of polarization phenomena and was first observed by Helmholtz (8) and by Fromme (19). It is considered to be due to the fact that the gas which is deepest down in the pores diffuses out very slowly, and is at a greater concentration, corresponding to the greater potential exhibited. When the current is turned on, the gas in the surface separates the electrolyte from the gas farther down in the pores, and the potential shown is that of the surface gas. When this has escaped the electrolyte penetrates to the more concentrated gas, and the potential of the latter shows itself again.

These results show that occluded hydrogen may raise the potential of nickel considerably above 0.48 volt.

Since, in the deposition of nickel, hydrogen is always co-deposited, the effect of this hydrogen upon the deposition potential of nickel will be considered next.

[1] This probably forms a sodium-nickel alloy, the subsequent decomposition of which leaves the nickel in a very porous condition.

The first determination of the least cathode potentials with which nickel is deposited was made by Kuester (6). He found nickel to be deposited out of neutral N/1 nickel sulphate solution at 0.80 volt. With acidified, or with more dilute, solutions a higher potential is required. Coffetti and Foerster (7) found that nickel was deposited out of N/1 nickel sulphate solution acidified with N/400 sulphuric acid under the following conditions: current density, 0.113 ampere per 100 sq. cm.; cathode potential, 0.903 volt; current yield, 20 per cent. One may infer from their article that they were unable to deposit nickel at a lesser potential.[1] I found that nickel may be deposited out of neutral N/1 nickel sulphate solution on a sheet nickel cathode at considerably lower potentials. The results attained with the lowest potentials employed are as follows:

(*a*) Perfectly neutral N/1 nickel sulphate solution was employed in the apparatus described at length in the first part of the following paper on "The Behavior of the Nickel Anode." The large pole was used for the cathode, and the anode was placed inside of the porous tube. The current density at the cathode was 0.026 ampere per 100 sq. cm., and the cathode potential, 0.75 to 0.76 volt. The amount of deposit obtained is 0.1265 gram, which represents 55 per cent of the current used. In a second trial under the same conditions, 0.110 gram were deposited, representing 45 per cent of the current used.

(*b*) Since the potential of nickel in N/1 nickel chloride is approximately the same as in N/1 nickel sulphate solution, the deposition potential for nickel chloride solution should not be essentially different from that for sulphate solutions. The apparatus employed for these determinations (which is the same as that employed for the depositions at higher temperatures described below) was unintentionally different from that employed above. A current density of 0.05 ampere

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[1] Coffetti and Foerster (7) state that Kuester (6) found the least deposition potential of nickel out of N/1 nickel sulphate solution to be 0.90 volt, and they argue that this value gives a remarkable support to Muthmann and Fraunberger's value, 0.88 volt. If their reference is correct, then their quotation is erroneous and the argument has no basis.

per 100 sq. cm. gave a cathode potential of 0.675 volt. The amount of the deposit obtained was 0.022 gram, which represents 23 per cent of the current used. In a second experi-
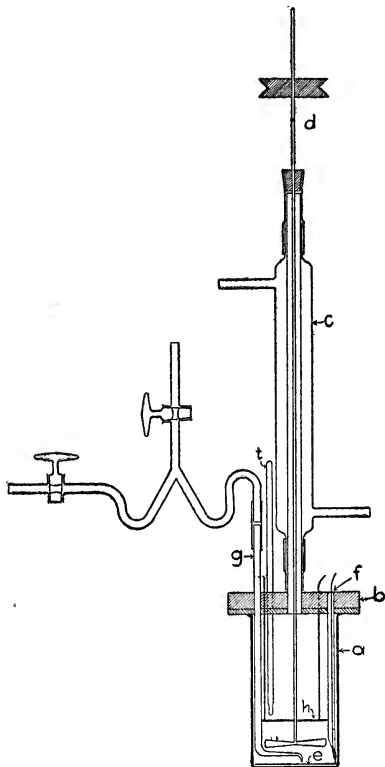
Fig. I.

ment the potential was 0.69 volt and the current yield 26 per cent.

The deposits obtained in the preceding experiments were all of dull appearance, and hence were open to the suspicion of being deposits of basic salts rather than of the metal. However, such films would have introduced surface resistances and would have influenced the potential. Since no such influences were observed we may conclude that the deposits were essentially of pure metal.

At best these results leave a wide gap between the equilibrium potential, 0.48 volt, and the least deposition potential observed with sulphate solutions, 0.75 volt. This appears to be an objection to the acceptance of 0.48 volt as the correct value for the equilibrium potential. However, the following deposition experiments at higher temperatures will help to remove this objection.

Figure I. shows the apparatus employed in these determinations. *a* is a thin porcelain beaker, 8 x 20 cm.; *b*, a well-fitting cover of soft sheet rubber reinforced with a piece of hard rubber; *c*, a small condenser; *d*, a long glass rod, to the lower end of which two glass turbine vanes are attached and which is fitted near its upper end with a pulley; *e*, a circular sheet nickel electrode with a long narrow strip, *f*, extending through a glass tube which insulates it from the solution; *g*, tube providing connection with the calomel electrode—the lower end is drawn out to a fine capillary; *h*, the upper circular sheet nickel electrode—held in place by two narrow strips of nickel; *t*, a thermometer. The tube *g* was left sufficiently loose in the cover so that potentials at different points of the lower electrode might be observed. The curves in the tube connecting with the calomel electrode prevented a mixing of the liquids by convection currents. The lower electrode was used for the cathode. Before weighing it, it was washed first with water, then with alcohol, and dried by gentle warming. The beaker and contents were heated in a large water bath. The results obtained are given in the following table:

Number.	Solution.	Temperature.	Ampere per 100 sq. cm.	Amount of deposit in grams.	Yield in per cent of current.	Cathode potential.	Remarks.
1	N/1 NiSO₄	98°	0.25	0.2083	90	0.59–0.63	Plate bright
2	"	98°	0.25	0.2310	88	0.59–0.63	"
3	"	98°	0.05	0.0375	90	0.53–0.59	"
4	"	98°	0.05	0.0403	91	0.53–0.59	"
5	"	80°	0.05	0.0192	65	0.73	Deposit dull
6	"	80°	0.05	0.0401	68	0.74	"
7	N/1 NiCl₂	98°	0.05	0.0598	78	0.51–0.53	"
8	"	98°	0.05	0.0461	75	0.51–0.53	"

In Nos. 1 to 4 the cathode potential fell rapidly to 0.47 volt when the circuit was opened. The equilibrium potential at 98° is between 0.42 and 0.44 volt.

The results with N/1 nickel chloride solution are added merely to indicate that there is nothing peculiar in the behavior of nickel sulphate as contrasted with other salts. Since the nickel chloride is hydrolyzed when cold the solution was filtered (cold) before it was used.

The lowest deposition potential with N/1 nickel sulphate solution shown above is still at least 0.09 volt above the corresponding equilibrium potential, but it is much nearer the latter than is the case at ordinary temperatures. And since at 98°, even with as small a current density as 0.05 ampere, nickel is deposited in the main (90 per cent), the deposition of nickel takes place even with lesser current densities and cathode potentials. The general relation of the cathodic polarization to the current density at 98° is here given.

N/1 Nickel Sulphate at 98°.

Current density in amps. per 100 sq. cm.	Cathodic polarization.	Current density in amps. per 100 sq. cm.	Cathodic polarization.
0.004	0.50	0.075	0.60
0.008	0.525	0.150	0.61
0.015	0.555	0.375	0.625
0.040	0.565	0.750	0.65

The curve plotted from these figures is given in Fig. II., in which are shown, for comparison, the curves for the deposition
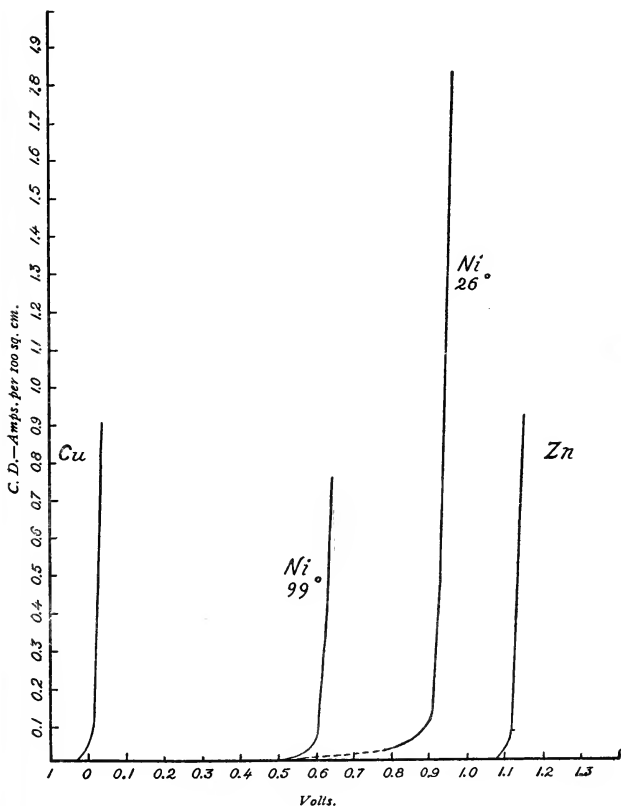
Fig. II.—Cathodic polarization values.

of copper out of N/1 copper sulphate, zinc out of N/1 zinc sulphate, and nickel out of N/1 nickel sulphate solution,[1] all

[1] Most of the data for the last three curves are from Coffetti and Foerster's paper (7).

three at ordinary temperatures. It is seen that the main portions of all the curves, with current densities above 0.1 ampere, are almost parallel. They are nearly straight lines—possibly logarithmic curves, as they should be in accordance with Nernst's formula. This part of the curve for nickel sulphate at 25° had given much support to the idea that the equilibrium potential of nickel might be 0.88 volt because when this curve is continued similarly to the curve for copper and zinc the point corresponding to 0.0 current would be 0.88. In the same way the upper part of the curve for nickel at 99° would lead to another potential, about 0.55 volt. Thus it appears as though the deposit obtained from nickel solutions with larger current densities is a metal with a *particular potential*, which varies with temperature. However, with small current densities the curves turn suddenly so that the continuation makes a very small angle with the "potential" axis. The data for some well-established points on these portions of both curves are given by my experiments above. The continuation of this portion of the curve for 99° shows that the point corresponding to 0.0 current is approximately at 0.44 volt, and thus indicates that the equilibrium potential of Ni–N/1 nickel sulphate solution at 99° C. is correctly located.

It follows that at ordinary temperatures either the equilibrium potential is much higher, or some special cause operates to prevent the deposition of nickel except with cathodic potentials 0.2 to 0.3 volt above 0.48 volt. Such an influence of temperature upon the equilibrium potential would be unique and surprising and as the behavior of the nickel pole in all other respects points to 0.48 volt as the equilibrium potential, we will dismiss the first possibility stated above and endeavor to point out the "cause" of the "gap" between 0.48 volt and the least deposition potential.

In the literature on the subject of deposition potentials is found the idea that the phenomenon is due to a "deposition resistance," an idea advanced by Kuester (6 and 21) in connection with the deposition of iron-nickel alloys. He and Toepfer (22) found that with very small current densities a

trace of nickel alone may be deposited out of the solution containing both iron and nickel, but with greater current densities iron is codeposited in a greater proportion than its proportion to nickel in the solutions. Since the deposition potential of iron out of a separate solution under the same conditions is at least 0.1 volt higher than the deposition potential of nickel, this preponderance of iron over nickel in the deposit is very surprising. Kuester reached the conclusion that the resistance to the deposition of iron is greater than that to the deposition of nickel. But the proof he advances, which involves the use of nickel and zinc, is not convincing, for these two metals differ considerably in their excess tensions and this was not taken into account by Kuester.

Foerster (11) has recently set forth again the idea of *deposition resistance*. He shows that at higher temperatures the "cathode potential"–"current density" curves of *cyanide* and of *ammoniacal* solutions of copper, zinc, silver, and cadmium salts diverge less from the "current density" axis than they do at lower temperatures, and he argues that this influence of temperature indicates that we have to deal with a chemical or "reaction resistance." The application of this idea of deposition resistance to the deposition of nickel is also being considered by Foerster, but in this he has reached no decision so far.

Though this idea of "resistance" has much to command it, I am of the opinion that the cause of the "gap" is found in special *potential* relations which exist between the deposit and the solution. The possibility of such novel relations first revealed itself in connection with a study of the deposition of nickel-zinc alloys, which I carried out in conjunction with Mr. A. Hirsch (23 and 24).

The same surprising relations between the composition of the solutions and the alloy deposited therefrom which is shown by nickel and iron is shown much more strikingly by nickel and zinc. The ratio Zn: Ni in the alloy is from 4.3 to 24 times the ratio Zn: Ni in the electrolyte. This preponderance of the deposition of zinc over that of nickel cannot be due es-

sentially to a difference in "reaction velocity," for the following reasons: With very small current densities nickel should be deposited free from, or with very little, zinc, because the deposition potentials of the two metals singly are 0.25 to 0.30 volt apart; but deposits obtained with the least possible current density contained never less than 30 per cent zinc and usually nearly 80 per cent. A striking example is here given in detail (24): Current density, 0.1 ampere per 100 sq. cm.; current yield, 26 per cent; amount of deposit, 0.0326 gram; ratio (*a*), *Zn*:*Ni in alloy*, 4:1; ratio (*b*), *Zn*:*Ni in electrolyte*, 1:6; ratio *a*:*b*, 24:1.

An insight into the underlying causes that produce these results was obtained through the following two experiments:

(1) *The Determination of Least Cathodic Deposition Potential upon a Mercury Cathode.*—The mercury cathode prevented the evolution of hydrogen. Of course, nothing is known concerning the composition of the deposits formed under these conditions, and the potentials observed are all somewhat irregularly lower than those which would have been observed on other poles (*e. g.*, platinum), yet it may be claimed that the picture of results obtained shows points which must have corresponding points in the normal state of affairs. The curve of the results is shown in Fig. III.
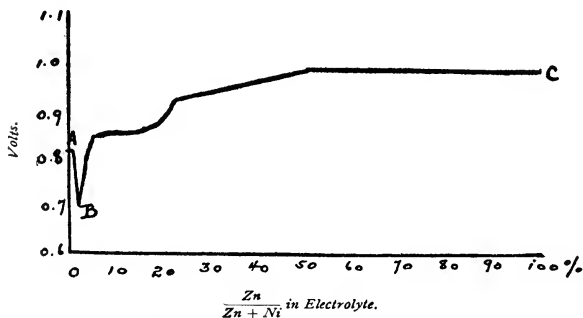
Fig. III.—Least cathode potential for deposition of nickel-zinc alloys.

A surprising state of affairs revealed itself: Nickel, when present alone, shows one particular least deposition potential, but when zinc is present in any amount above 7 per cent (approximately), then no current flows—nothing is deposited—until a higher potential, varying with the composition of the solution, is reached. This shows that a metal in the presence of a second metal may not be deposited on a cathode which is at a higher potential than that at which the metal, if present by itself, would be deposited. This is not due to a resistance, because as soon as the deposition potential of the solution is exceeded, the deposition takes place without any noticeable hindrance. It is probable that deposition can take place only when the potential of the resulting alloy is exceeded by the cathode potential.[1]

(2) *The Determination of the Relation of Zinc to Nickel in the Solution which is in Equilibrium with Any Particular Sample of "Nickeled" Zinc Dust.*—With one such sample equilibrium was attained when the solution contained 2.2 per cent of nickel by equivalents. The total concentrations of the solution ranged from two normal to half normal, and at the beginning some of the solutions contained less and others more than this proportion of nickel. From the Nernst formula for the potential of a pole, it follows that these metals in the alloy must have very nearly the same solution tension. Since the alloy consists mainly of zinc with only a small amount of nickel, it follows that the solution tension of nickel in this alloy is much greater than that of pure nickel. Thus it appears that a metal, when alloyed, may have its potential raised. Naturally, it will then require a higher deposition potential.

Of the two ideas set forth in the preceding pages, that of a *special potential* relation accords better with the facts observed

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[1] The composition of the alloy is determined by the mutual solubility—or alloying tendency—of the two metals, and this is probably the fundamental cause of the deposition of the large percentage of zinc. This view accords with well-established principles: For instance, in Fig. III. the portion of the curve A to B corresponds to the formation of nickel with gradually increasing amounts of zinc dissolved in it, and hence to falling potentials; the portion C to B corresponds to the formation of zinc with gradually increasing amounts of nickel dissolved in it, and hence also falling potentials. The two curves cross in B.

in the deposition of nickel than the idea of a *reaction resistance*. This becomes evident when the curves for the deposition of nickel and other metals (see page 225) are recalled. It was pointed out in connection with the curves for nickel that the portions with current densities above o.1 ampere per 100 sq. cm. are of such a form as to indicate that the deposit obtained at any one temperature is a metal with a definite potential, which is less at higher temperatures. Since hydrogen is codeposited with nickel, and the deposits exhibit potentials above that of nickel, it is quite likely that, with large current densities, the deposited metal takes up the maximum amount of hydrogen which it can hold at that temperature and hence the deposit exhibits a maximum potential (o.88 volt at ordinary temperatures; o.55 volt at 99°). Schoch and Hirsch found (23) a similar relation in the deposition of zinc-nickel alloys; with increasing current densities, the composition of the alloys obtained finally becomes constant with a maximum per cent of zinc. With current densities less than o.1 ampere, the nickel-hydrogen particles separated from the solution contain (probably) less hydrogen than the maximum amount and hence they may be deposited at lower potentials. The lowest limit of potentials that can be thus obtained is probably fixed by the composition of the solution—just as was found to be the case with the nickel-zinc solutions— and hence this lower limit may be considerably above the equilibrium potential of nickel—in a sense it has no direct connection with it.

Thus we see that the idea of potential relations similar to those found with nickel-zinc alloys fits every known detail concerning the deposition of nickel.

Though there may be many possible explanations involving the idea of a reaction resistance, yet it seems to me that none will be able to overcome the fundamental difficulty, namely, that with potentials below o.88 volt the resistance would have to be very great, while with potentials above o.88 volt it would be zero or very small. Such a *sudden* change is incompatible with the idea of a *resistance* influence.

This "proof" of a special potential relation is probably in-

complete. Whether the "gap" is due to a *resistance* or to a *potential* phenomenon is still an open question, but that the existence of the "gap" should be an argument against accepting 0.48 volt as the equilibrium potential of nickel has, I think, been rendered unlikely.

Summary.

1. The potential of nickel in N/1 nickel sulphate solution is 0.48 volt.

2. This is the true reversible potential, because it is attained from both sides as the final point of equilibrium.

3. Occluded hydrogen raises the potential of nickel. The deposition of the metal does not take place except at potentials 0.2 to 0.3 volt above 0.48 volt because hydrogen is codeposited and, in general, deposition cannot take place until the potential of the particles to be deposited is reached.

In conclusion, I wish to express my appreciation of the help which Mr. H. S. Bonham, of this laboratory, has given me in some of the experimental work.

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THE BEHAVIOR OF THE NICKEL ANODE AND THE PHENOMENA OF PASSIVITY.[1]

BY E. P. SCHOCH.

A number of investigators have studied the behavior of the nickel anode in connection with "passivity." But no one has studied it with the view of locating the equilibrium potential, and no one appears to have started his observations from any particular potential.

Hittorf (4) studied nickel briefly in connection with his general investigation of passivity. His work is, in a sense, mainly qualitative, and since his results are now found in text-books, it is unnecessary to repeat them here.

Le Blanc and Levi (5) determined the extent of action of different electrolytes upon nickel anodes. They noted also the effect of temperature. The effect of current density was not studied in detail, and the anode potential was observed only approximately by noting the voltage drop between the poles. They found that hydrogen and halide ions increase the anodic solution of nickel markedly, also, that increase of temperature increases the action of electrolytes on the nickel anode.

Foerster and Piguet (1) determined the anodic potential

[1] See footnotes 1–3, p. 208 of preceding paper on "The Electromotive Force of Nickel."

with which oxygen is evolved from 2 N potassium hydroxide solution on a nickel anode in comparison with anodes of platinum and iron. They found that oxygen is evolved on nickel at a lower potential than on iron (difference, 0.12 volt) and at much lower potential than on smooth platinum (difference, 0.32 volt). They also noted in this connection that no determinable quantity of nickel is dissolved, and the surface remains perfectly bright—no oxide is formed.

E. Mueller and Spitzer (2) determined the conditions under which nickel oxide is precipitated out of a solution upon a platinum anode, and then determined the potentials at which oxygen is evolved on platinum, nickel, and nickel oxide deposited on platinum. They had found that with cobalt and iron, respectively, oxygen is evolved on the metal at the same potential as on the oxide, and at a much lower potential than upon platinum. With nickel, however, the following figures were obtained:

	Volts.
Platinum	1.416
Nickel	0.900
Nickel oxide	0.540

Hence, the same statement cannot be made for nickel as for cobalt and iron.

Fredenhagen (6) determined the "current-density: anode-potential" curves of nickel in N/10 and N/1 sulphuric acid and N/1 hydrochloric acid, as obtained with *increasing* and *decreasing applied electromotive forces*, respectively. With sulphuric acid, he finds a sharp turn in the curves with increasing applied electromotive forces, which indicates that the anode has suddenly become almost insoluble. In the curve obtained with decreasing applied electromotive forces the "turn" occurs at another point. With N/1 hydrochloric acid and with sulphuric acid at high temperatures there is no such critical turn in the curves, and they bend away much less from the current density axis than the curves for sulphuric acid at ordinary temperatures.

Sackur and Alvares (7) studied the behavior of the nickel anode in the same manner as Fredenhagen. They worked

with from 5 N to 0.15 N sulphuric acid and found an approximate proportionality between the concentration of the hydrogen ions and the "critical current density" which just precedes the "turn" to passivity. Then they tried the effect of the addition of halide ions and found it also proportional to their concentration. Finally they found that passive nickel is still slightly soluble.

The purpose of my own experiments was to start with the nickel anode under equilibrium conditions—*i. e.*, in neutral nickel sulphate solution, and at the equilibrium potential—and to study its behavior as these conditions are gradually departed from.

In designing the apparatus the following points had to be considered:

(*a*) To remove and exclude oxygen, and to prepare the pole—*i. e.*, the surface of the metal—in as definitely reproducible a manner as possible.

(*b*) To stir the liquid next to the anode surface so effectively that any further increase in the rate of stirring produces no noticeable effect. This, with a relatively large volume of solution, insures constant composition of the solution next to the anode.

(*c*) To use a large anode surface because many of the current densities employed must be very small, and with a small anode surface, irregular influences may easily distort the results.

(*d*) Since many of the current densities to be employed are of the dimensions of "rest-currents"—*i. e.*, currents depending upon the convection of hydrogen to the anode—and since the potential of nickel may be influenced by hydrogen, the introduction of hydrogen into the electrolyte had to be absolutely prevented.

The apparatus designed with these points in view is shown in Fig. I. *a* is a large test tube, 5 x 25 cm.; *b*, a cylinder of sheet nickel which fits closely into the test tube (area of inner surface, 270 sq. cm.); *c*, a rubber stopper; *d*, a porous earthenware tube, 2 x 25 cm. (Pukall filter tube), open at both ends; *e*, a rubber stopper closing *d*; *f*, a glass tube; *g*, a stirrer of glass

rod (this fits closely into the glass tube f); h, a short piece of rubber tubing; i, a pulley; k, a glass tube with one end drawn to a capillary, which serves to connect the calomel electrode (the two liquids meet at the Y joint, and the curves prevent the convection currents from mixing the liquids); l, a thermometer (not shown—it is inserted through c); m, a thin lead
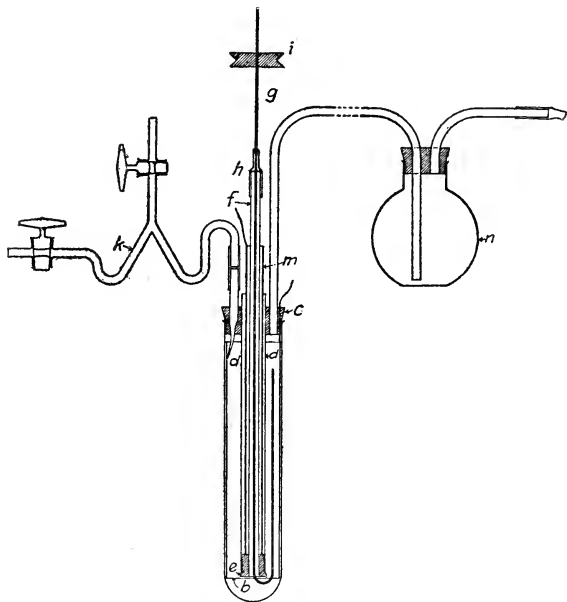
Fig. I.

pipe whose surface has been converted into lead peroxide (this serves as the cathode and eliminates the evolution of hydrogen); n, a flask which holds the excess of electrolyte (the level of the liquid in it is above the top of the test tube so that in the event of a leak anywhere air would not be admitted but liquid would be forced out through the leak).

In an operation, the test tube is nearly completely filled with the electrolyte, and a sufficient excess is poured into the flask with which the syphon connects. After the apparatus is properly closed and connected up, the liquids are boiled vigorously for several minutes, until with a slight lowering of the temperature and the condensing of the steam the test tube and syphon fill completely with the electrolyte. The stirrer is turned at a rate of about 200 revolutions per minute. With this apparatus and procedure the following results were obtained:

Electrolysis of N/1 Nickel Sulphate Solution, at 25°.—Table of Characteristic Polarization Values (See *b* below).—

Curve I.

Current density[1].	Potential[2].	Current density.	Potential.
0	0.475	12	0.27
0.04	0.47	16	0.222
0.08	0.463	24	0.123
0.12	0.457	32	0.05
0.2	0.445	36*[3]	. . . . .
0.4	0.432	. .	. . . . .
0.8	0.42	14	—0.885†[4]
2.0	0.39	24	—1.06 †
4.0	0.36	185	—1.131 †
8.0	0.315	. .	. . . . .

Special observations on the electrolysis with neutral N/1 nickel sulphate solution:

(*a*) The potentials obtained with current densities less than 4 milliamperes are readily reproducible; *i. e.*, approximately the same potentials are obtained with increasing or decreasing current densities as long as the limit 4 milliamperes has not been reached. This behavior is commonly considered to be *normal* anodic behavior.

(*b*) Beyond this limit the results are no longer reproducible; if the current density applied is not excessive, then the po-

[1] All current densities are expressed in *milliamperes* per 100 sq. cm.

[2] All potentials spoken of in this paper are *anode* potentials, unless it is specially stated to be otherwise.

[3] In this and the following tables the current density with which passivizing sets in immediately is marked by an asterisk (*).

[4] The potentials shown by the anode in the passive state will be marked thus (†).

tential of the pole may become stationary within a few minutes and may remain so for a long period (30 to 50 minutes and even longer). With excessive current densities the potential will continue to drop indefinitely—until the evolution of oxygen sets in. However, the stationary potential obtained with the same current density has different values depending upon the previous treatment: *e. g.*, the amount of preceding
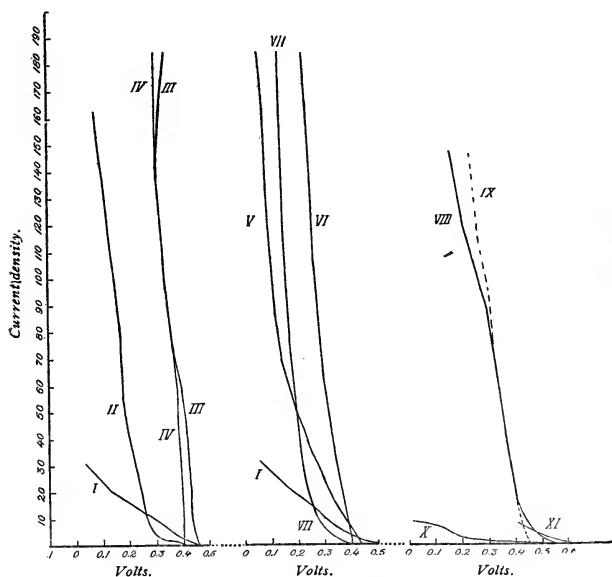
Fig. II.—Nickel anode-polarization values.

electrolytic action, the periods of rest, etc. In short, the values are not reproducible. Thus with a current density = 7.4 the following two stationary conditions were maintained for one hour: one at 0.32 volt, and the other at 0.024 volt. If to a newly prepared pole a particular current density is applied until a stationary condition is reached, the two sta-

tionary conditions are often not attained in the same time, and the final potentials are not the same. Thus, with a current density = 11, the stationary potential attained in one case was at 0.123 volt and in another at 0.012 volt. These stationary potentials appear to be determined by the accidental conditions of the pole surface which result from the electrolysis.

This state of affairs requires the framing of an arbitrary rule for selecting the potential values corresponding to the different current densities. I found that satisfactory reproducible results are obtained when the current densities employed form an increasing series of values and the time of operation of any one current density is from $\frac{1}{2}$ to 2 minutes, approximately. All values for the curves in this part have been so obtained.

With this procedure the condition of the anode can be reliably identified—as will develop farther on—and hence these values are designated as characteristic polarization values.

(c) The chemical action which takes place as long as the potential for the evolution of oxygen has not been reached is a quantitative solution of the nickel. Thus, for example, in an electrolysis with neutral N/1 nickel sulphate solution in which the potential dropped as low as —0.17 volt for a part of the time (but no lower) the anode lost 0.1100 gram during the whole operation, while the current used required a loss of 0.1058 gram—a fair agreement. Other trials have confirmed this result.[1]

(d) There is neither a critical voltage nor a critical current density which terminate the active and mark the beginning of, or change to, the passive state. Thus a current with current density = 24 and an initial potential of 0.123 volt, when allowed to continue for 15 to 20 minutes, produced the condition which we shall call *passivizing*; *i. e.*, even a very small current density produces steadily lower potentials until finally the evolution of oxygen begins. On the other hand, with a current density = 32 and an initial potential of 0.050 volt passivizing did not set in for several minutes. Again with a current density = 7.4 and an initial potential of 0.024 volt, passivizing did not set in even during one hour, which might be considered as showing

[1] See also the results obtained by Byers: J. Am. Chem. Soc., **30,** 1740.

that the pole is in the active state. Yet when the current was raised to current density = 11, passivizing set in immediately. There is evidently no one value which alone marks the beginning of "passivizing." And just as the "stationary" conditions considered under (b) depend upon the previous treatment of the electrode, so the conditions for passivizing depend upon the previous treatment.

Furthermore, the change of potential preceding and during "passivizing" may be made to progress as slowly or as rapidly as desired by regulating the current density. Apparently no sudden change is wrought in the anode when "passivizing" sets in.

Fredenhagen (6), Le Blanc (5), and Sackur (7) observed, when using dilute sulphuric acid as the electrolyte, that the change, in voltage, from active to passive state takes place *suddenly*, and Sackur even speaks of a particular critical current density. Hence I consider it important to point out that with nickel sulphate no such state of affairs exists.

(e) Whenever the current is discontinued the potential of the pole begins to rise immediately. In general, the rate with which it rises is less as the extent of the preceding electrolysis was greater, and the accompanying potentials were lower. If electrolysis has lowered the potential no further than o volt (approximately) then the potential will rise rapidly to very nearly the former maximum value. If electrolysis has been more extensive, and has produced lower potentials, there will be a noticeable pause in the neighborhood of 0.3 volt as the potential ascends. It should be noted that this coincides with the so-called "air" potential.

Even after the pole has regained the equilibrium potential, the surface of the pole has not returned to its former state, as is shown by the fact that at the same potentials, the current densities now supported are much smaller than those supported by the newly prepared pole. This same condition obtains all the more if the pole did not regain even the equilibrium potential.

In the course of time, however, the pole regains its former state gradually. The change can be enormously accelerated

by boiling the pole with its liquid, as is done at the beginning of each operation. With neutral N/1 nickel sulphate solution, a maximum of five minutes' boiling restores the former condition of the surface, irrespective of the amount of electrolysis that has preceded. *It is notable that the surface thus prepared gives the same polarization curve not only with the same piece of sheet nickel after it had been subjected to electrolysis, but also with different pieces of nickel.*

However, this rate of "return" of the surface to its "normal" state is much slower if free nickel hydroxide is floating in the liquid. Thus, to a nickel pole with which a series identical with that for Curve I. had been obtained, and which, after reboiling, had just given the same series, enough potassium hydroxide was added in the anode compartment to precipitate one-tenth of the nickel in solution. After reboiling and cooling it gave the following series:

Current density:	0	3.7	7.4	11.1
Potential:	0.436	0.295	0.197	—0.098

It is evident that the surface has not regained its original state.

Electrolysis with N/1 Nickel Chloride Solution, at 25°.—Table of Characteristic Polarization Values.—Curve II.

Current density.	Potential.	Current density.	Potential.
0	0.418	11.1	0.267
0.04	0.401	18.5	0.246
0.08	0.387	37.0	0.208
0.1	0.381	45.0	0.190
0.18	0.373	75.0	0.175
0.37	0.363	90.0	0.155
0.74	0.344	164.0	0.081
1.11	0.336	370.0	—0.049
1.48	0.327	534.0	—0.098
2.22	0.319	904.0	—0.160
2.96	0.307	1274.0	—0.221
3.7	0.298	1808.0	—0.339
7.4	0.276	2590.0	—0.393
....	.....	3700.0	—0.541

Further remarks on electrolysis with N/1 nickel chloride solution:

(*a*) The solution was filtered cold to remove the basic salts which had been formed by hydrolysis.

(*b*) Frequently it is impossible to obtain any potentials above 0.32 volt when the solution is stirred. In that case, current densities less than 2.22 will produce no lowering of the potential, and the potentials observed with larger current densities will be the same as those obtained in the series above. If the pole is allowed to rest, without stirring, it attains the equilibrium potential (0.418) in almost every instance, but frequently the potential will drop to 0.32 volt again as soon as the solution is stirred.

(*c*) It is seen that there is a sharp turn in the curve at current density = 0.4, which indicates a change in the chemical process.

(*d*) Upon opening the circuit the potential returns quickly to the maximum value (0.32), irrespective of the extent of electrolysis. This shows that the behavior of the anode in chloride and sulphate solutions is essentially different at all except the highest potentials. The potentials in N/1 nickel chloride solution are approximately reproducible, and they soon attain, with any one current density, a stationary condition, indicated by the constancy of the potential. Thus, with current density = 50 the potential shown after 20 minutes and maintained for 3½ hours was 0.17 volt.

Electrolyses at Higher Temperatures—96°.

3. *N/1 Nickel Sulphate—Curve III.*		4. *N/1 Nickel Chloride—Curve IV.*	
Current density.	Potential.	Current density.	Potential.
0	0.442	0	0.405
0.37	0.44	0.37	0.405
0.74	0.44	0.74	0.405
1.0	0.44	3.7	0.405
1.9	0.436	7.4	0.399
2.6	0.436	11.1	0.393
3.7	0.43	18.5	0.393
7.4	0.424	25.9	0.387
18.5	0.418	37.0	0.375
37.0	0.406	55.5	0.369
55.5	0.393	74.0	0.356
74.0	0.363	111.0	0.325
185.0	0.319	185.0	0.303

Further remarks on electrolyses at higher temperatures:

(*a*) Upon opening the circuit, the potential "jumps" back to the value corresponding to zero current, irrespective of the extent of the electrolysis that has taken place.

(*b*) The values above are but *slightly* higher than the values shown during prolonged electrolysis. Thus, with nickel sulphate electrolyzed for three hours with a current density = 50, the potential remained practically steady at 0.39 volt, while with a current density = 125 it showed 0.34 volt during two hours. With nickel chloride electrolyzed with a current density = 50, the potential remained at 0.36 volt during three hours.

Hence the behavior shown by the nickel anode in the solutions above at 95° C. may be said to be *normal*, both with reference to the chemical actions (which consist of the quantitative solution of the metal) and to the electrical behavior, as set forth above.

Electrolyses with Acidified N/1 Nickel Sulphate Solution.

5.—With N/100 Sulphuric Acid—Curve V.		6. With N/10 Sulphuric Acid—Curve VI.	
Current density.	Potential.	Current density.	Potential.
0	0.418	0	0.393
3.7	0.393	3.7	0.375
7.4	0.369	7.4	0.366
18.5	0.319	18.5	0.338
25.9	0.270	37.0	0.313
37.0	0.221	55.5	0.289
55.5	0.172	111.0	0.246
74.0	0.123	185.0	0.204
92.5	0.098	296.0	0.166
111.0	0.085	370.0	0.141
129.5	0.070	555.0	0.095
148.0	0.065	740.0	0.046
166.5	0.057	1480.0	0
185.0	0.046	1850.0	—0.073
222.0	0.043	2220.0	—0.123
259.0	0.009	2580.0	—0.246
296.0	0	2960.0*	. . . . .
333.0	0	. . . . .	. . . . .
370.0	—0.020	2960.0	—1.722†
555.0	—0.028		
529.0*	. . . . .		
. . . . .	. . . . .		
629.0	—1.648†		

When the current is interrupted, the potential returns promptly to the value corresponding to zero current. This takes place even after oxygen has been evolved (at the lowest potentials given).

Electrolyses with N/1 Nickel Chloride Solution Acidified with N/10 Hydrochloric Acid.—Curve VII.

Current density	0	3.7	7.4	19.5
Potential	0.393	0.319	0.270	0.233
Current density	37.000	74.000	185.000	
Potential	0.204	0.172	0.123	

This series of values does not differ markedly from the series obtained with the neutral solution.

In order to be able to study the effect of alkaline solutions in the electrolysis with nickel anodes I substituted $N/1$ potassium sulphate for $N/1$ nickel sulphate solution and ascertained the difference in effect due to this change.

Electrolyses with N/1 Potassium Sulphate Solution.—Table of Characteristic Polarization Values.—Curve VIII.

Cur. density	0	0.74	1.85	3.7	7.4	18.5
Potential	0.571	0.524	0.492	0.467	0.442	0.393
Cur. density	37.000	74.000	111.000	148.000	185.0*	
Potential	0.369	0.319	0.221	0.155	....	

Notes on electrolysis with $N/1$ potassium sulphate solution:

(a) The passivizing drop is very sudden. Since this *sudden* drop is always observed with electrolytes for which a large current density is required to produce passivity, it is probably due entirely to the large current and hence it is an *unessential* characteristic.

(b) The surface is "impaired" by electrolysis with potassium sulphate just as with nickel sulphate—*i. e.*, it will stand less current density than before at the same potentials. After the current is interrupted, the pole regains the higher potentials just as slowly as it did with nickel sulphate. Boiling restores the surface completely.

(c) Much greater current densities can be sustained by the anode at any one potential in potassium sulphate than in

nickel sulphate solution. This is due to a peculiar condition of the surface produced by interaction between the metal and the solution. The same surface, after it was thus effected, produced in N/1 nickel sulphate solution the following characteristic polarization values (see Curve IX.—dotted):

Cur. density	0	1.11	2.22	3.7	7.4	18.5
Potential		0.467	0.442	0.439	0.436	0.418	0.393
Cur. density	37.0	74.0	111.0	148.0	185.0*	
Potential		0.356	0.319	0.270	0.231	....	

This shows that the anode sustains larger current densities in nickel sulphate just as well as in potassium sulphate solution, hence the difference is not due to the liquid. The pole was next subjected to electrolysis in nickel sulphate solution with current density = 3.7 and a potential of 0.197 volt for five hours, with the view to removing the affected surface. Then the apparatus was refilled with another portion of N/1 nickel sulphate solution, which was then boiled and cooled; after this the original characteristic polarization values were obtained again, which shows that the effect is superficial.

It is likely that a nickel-potassium alloy is formed by the interaction of nickel and the solution. The existence of such an alloy has been demonstrated by Siemens (8). That such an action occurs is also indicated by the fact that nickel dissolves extensively in potassium sulphate solution.

Electrolyses with N/1 Potassium Sulphate Solution Alkaline with N/10 Potassium Hydroxide.—Table of Characteristic Polarization Values.—Curve X.

Current density.	Potential.	Current density.	Potential.
0	0.565	11.1	—0.369†
0.37	0.430	18.5	—0.418†
0.74	0.282	25.9	—0.442†
1.11	0.240	37.0	—0.454†
1.85	0.196	55.5	—0.467†
2.59	0.180	74.0	—0.473†
3.7	0.166	111.0	—0.492†
5.55	0.135	148.0	—0.51 †
7.4	0.073	185.0	—0.524†
9.25	0.024	370.0	—0.590†
11.1*			

Several minutes elapsed before the potential corresponding to current density = 0.37 became "steady."

The passivizing "drop" which began with current density = 11.1 was very slow. With the negative potentials above, oxygen is discharged. When the current is interrupted the potential of the pole rises very *slowly*. At the end of the above determination the pole was boiled and cooled and the series of values then obtained showed that the pole had not regained its original condition.

Electrolyses with N/10 Potassium Hydroxide.—Curve XI.

Current density.	Potential.	Current density.	Potential.
0	0.639	11.1	—0.270†
0.74	0.590	14.8	—0.319†
1.85	0.543	18.5	—0.344†
2.6	0.528	26.0	—0.369†
3.7	0.467	37.0	—0.381†
7.4	0.405		
11.1*			

The passivizing drop is very slow. The return from the lower potentials also is extremely slow.

The following general conclusions can be drawn from a comparison of the results obtained with the different electrolytes:

(1) The extent of the "impairing effect" wrought by larger current densities upon the anode surface is roughly proportional to the concentration of hydroxyl ions in the electrolyte.

(2) The impairing of the surface in neutral and alkaline solutions may be effected as gradually as may be wished, and this process, as well as the change in potential, is perfectly *continuous* up to the potential with which oxygen is evolved.

(3) The return to high potentials takes place at a rate roughly proportional to the concentration of hydrogen ions in the electrolyte.

I wish to add here that these electrolytic actions produced no noticeable oxide film on the anode.

From (2) above it may be seen that by electrolysis at potentials *above* the discharge potential of oxygen the anode surface may be gradually *saturated* with oxygen—hence the

"impairing effect" is due to discharged oxygen. Evidently this discharge of oxygen begins as soon as the current densities exceed a *very* small limit.

(1) and (2) indicate that the proportional discharge of oxygen with any one current density is greater with alkaline than with neutral solutions, and less with acidified solutions.

I shall now proceed to a general discussion of the facts before us with a view to pointing out their theoretical relations.

As the behavior of the nickel anode in both sulphate and chloride solution with very small current densities is markedly different from the behavior with large current densities, it is likely that the changes which take place under these conditions are different. There is no reason why the change with small current densities should be any other than the ionization of the metal (with solution). The readiness with which the equilibrium potential is attained when the current is interrupted, and other similar indications, support this view. However, this conclusion is inseparably connected with the conclusion that the velocity of ionic solution of nickel at ordinary temperatures must be very small. The idea that metals may differ extensively in their velocity of ionization and that a very small velocity will produce *abnormal* anodic behavior was first advanced by Le Blanc (13). Many indications support the view that nickel has a small ionization velocity. Thus I found that the most concentrated nickel amalgam, when stirred vigorously so as to expose a great deal of new surface which cannot possibly be covered by a protecting film, does not show in $N/1$ nickel sulphate solution a potential above 0.1 volt, and if more current than that necessary for the electrometer is passed[1] the potential drops lower. It is readily seen that amalgamation may reduce the ionization velocity of a metal, and that with a metal which has, in the solid state, a very small ionization velocity, the reduction may produce a specially marked effect, such as that shown by nickel. However, the low potential may be due to a *specific* property of the amalgam. In this connection, the behavior of iron—the element most

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[1] In these trials, air was not excluded. However, it is not likely that the presence of air affected the result, because not the least rise of potential was observed on stirring the amalgam.

closely related to nickel—may be profitably considered. I found that iron amalgam in N/1 ferrous sulphate solution[1] shows a potential of 0.71 volt, which is identical with the potential of solid iron as determined by T. W. Richards and Behr (9). This renders it unlikely that amalgam formation should exert such an enormous specific influence as would be the case with nickel. On searching further in this connection we observe that iron appears to have a greater ionization velocity than nickel. Thus, from the work of Hittorf (4) and of Byers (10) it is seen that to passivize iron in sodium sulphate solution requires somewhat greater current densities than is necessary for nickel. It is also well known that dilute sulphuric acid dissolves iron more rapidly than nickel. Hence it is likely that the ionization velocity of iron is great enough so that even after amalgamation it ionizes rapidly enough to maintain its proper potential; and we may conclude that the inability of nickle amalgam to do so shows that nickel possesses a very small ionization velocity.

The following experiment also furnishes evidence on this point: A nickel anode and the liquid surrounding it (neutral N/1 nickel sulphate solution) were saturated with hydrogen gas and the current of hydrogen was continued during electrolysis. The anode loss that took place under these conditions was determined. The apparatus employed was that described on page 235 with the modification that to the lower end of the test tube was joined a narrow tube through which the hydrogen was introduced. The current density varied from 22 to 26 milliamperes, and the potential from 0.37 to 0.42 volt. The anode lost 0.0430 gram of nickel, while the cathode in the copper voltameter gained 0.4090 gram of copper; thus the loss of the anode is 11 per cent of the current. Hence the nickel ionized corresponding to a current density = 2.4, and in Table I., page 236, we find that nickel alone at the same potential (0.39 volt) supports about the same current density. Since the hydrogen had been passed through the apparatus prior to and during the time that the solution in

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[1] Air was carefully excluded in this determination, since it is essential that no ferric ions be present.

it was boiled it is unlikely that any (imperceptibly thin) film of oxide or a layer of oxygen could still be present on the nickel, and since, under these conditions, the nickel does not exhibit a greater ionization velocity than before, this small ionization velocity must be considered to be a specific property of the metal.

This idea is supported further by the influence of temperature. At 95° C., the nickel anode shows a " normal" behavior, which is evidently due to a greater ionization velocity. This is in accordance with our general experience, namely, that increase of temperature accelerates velocities of change.

If it is admitted that the action of the nickel anode at ordinary temperatures with small current densities consists of the direct ionization of the metal, then the different behavior with larger current densities is due to the complication produced by the simultaneous discharge of oxygen —because, as has been pointed out before, the discharge of oxygen also takes place at these high potentials, and there is no reason why the ionization of the metal should cease.

But what effect has the discharged oxygen? This question has been studied in connection with the general problem of passivity, and a review of the results obtained will help to answer the question here. Passivity is exhibited by many metals besides nickel, and has been the subject of many investigations. The recent extensive reviews of the literature of passivity by Freder agen (6) and Byers (10) render it unnecessary to make any comprehensive survey at this time. However, it appears to me that there are some facts which have been ommitted, or which have not been properly emphasized, and which may be profitably introduced here.

With the exception of Finkelstein (12) and W. J. Mueller (11)—whose views have apparently not been supported by other workers—and Le Blanc (13)—who suggested that passivity is a phenomenon of ionization velocity—all other investigators have considered that passivity is due to some effect wrought upon the surface of the anode by the discharged oxygen. Some think that the discharged oxygen remains essentially uncombined (Fredenhagen, Muthmann and Fraun-

berger), while many others believe that it forms an oxide film. The protective action of an oxide film is almost "self-evident"; however, to explain all the phenomena of passivity, detailed formulations have had to be elaborated. The two most extensive recently made are by Haber and Goldschmidt (15) and by Erich Mueller (16). They are entirely distinct in most of their essentials. In Haber's theory of "mobile pores" it is assumed that the oxide layer has holes in it which allow the metal to come into direct contact with the electrolyte and to dissolve (ionize!). With very thin (invisible) films—for which the theory is specially formulated—a constant destroying and reforming of the layer is assumed to take place. This results in a constant moving of the pores which expose the metal. Naturally, the relative extent of the areas of the pores and of the oxide cover may vary with the conditions. Erich Mueller's formulation was made in connection with his observation that a copper anode in sodium hydroxide solution exhibits all the characteristic signs of passivity. He observed that the anode is covered with a film, and obtained indications that the evolution of oxygen is due to the decomposition of copper peroxide.

Though all formulations of the oxide theory require that the oxide should have special properties—*e. g.*, it must conduct like a metal—yet the theory has gained much ground because special search has revealed the existence of many such oxides—*e. g.*, copper peroxide, by E. Mueller; platinum oxide, by Ruer (17); iron oxide, by Haber and Kaufmann (18)—and it cannot be denied that such oxides produce all the phenomena connected with passivity.

However, in many cases an oxide film is not apparent, and it has been impossible to detect it by the most refined methods. In such cases the oxide theory requires the assumption that only an imperceptibly thin film is formed. This film, to remain imperceptible, must either give complete protection, so that no more of the metal will be attacked, or it must be dissolved at the same rate at which it is formed. When we consider that many oxides—lead peroxide, iron oxide, aluminium oxide, etc.—do not

protect the metal under them against attack, and when we note the great differences that exist, not only in the solubilities of different oxides, but also of any one oxide, with slight variations in the electrolyte, we realize that this requirement should make the phenomenon much less frequent and less permanent than it is. To emphasize this, we need but point to the fact that a *thick* film of aluminium oxide is formed even in acid electrolytes; that Ruer (17) obtained in 6 per cent sulphuric acid a deposit of platinum oxide which dissolves readily in 50 per cent sulphuric acid, and yet the "passivity" phenomena exhibited by the platinum remain the same as in 6 per cent acid; that Thiel and Windelschmidt (3) found that visible films of nickel oxide might form on the anode at one moment and disappear entirely at the next; and that Foerster and Piguet (1) electrolyzed 2 N potassium hydroxide solution with a nickel anode for 48 hours, and at the end of that time the nickel was as bright as at the beginning.[1]

Altogether there are many special conditions which must be fulfilled before we can have an oxide film that will serve to protect the metal adequately; and it is difficult to believe that these special conditions always obtain. On this account Fredenhagen (14) has proposed his "free oxygen" or "oxygen alloy" theory. He assumes that the lesser solubility and lesser potentials of the anode are due to the fact that the metal is alloyed, or covered, with oxygen, and that the two react very slowly upon each other. He considers this "slow" reaction to be the primary cause of passivity—of the slight solution of the metal while in the passive state, and of the spontaneous return to the active state. Fredenhagen has answered successfully many objections that have been raised against his view.

For the present we are concerned with Fredenhagen's fundamental idea only—that a layer of oxygen gas may protect or

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[1] The optical proof of the absence of an oxide film is still a matter of dispute. Mueller and Koenigsberger (19) showed that the least amount of a film of lead peroxide formed could be readily perceived. The observations of Thiel and Windelschmidt (3) on nickel peroxide appear to confirm the result. However, Ruer (22) calculated that he had a layer of platinum oxide *much thinner* than that perceptible by optical methods. There are many other contradictions on this point in the literature, which will be found in the reviews mentioned.

separate a metal surface from the electrolyte, and react very slowly with the metal, although the latter is, in a sense, readily oxidizable. Without any reference to his theory as a whole, I wish to point out that this fundamental idea is well supported by what he has shown, and still more by the following facts.

(1) Sackur's (21) experiments show that a platinum anode polarized with oxygen is practically completely enveloped by it and isolated from the solution. He found that hydrogen which passed by such an anode was practically not oxidized, and since the oxidation of the hydrogen depends upon its being absorbed by the metal, the result indicates that the surface of the platinum is not in direct contact with the solution.

(2) The idea that the oxidation may take place slowly is strange at first sight because we unconsciously attribute the rapid and extensive formation of oxides occasionally observed to this effect. However, many such actions are precipitation actions and not direct oxidations.[1] Erich Mueller and Spitzer (2) have recently set forth the conditions and theoretical relations for such oxide formation. Oxides are readily formed on anodes in alkaline solutions, but they are usually formed when the conditions for their precipitation are fulfilled—*i. e.*, when the solubility product of the metal and hydroxyl ions is reached.[2] But when this is not the case—as in the absence of metal ions in solution, or when the anode does not dissolve—then an oxide is usually not formed. Thus I found that when a nickel anode is introduced into dilute sodium hydroxide while connected in such a way that it closes the current as it enters the electrolyte, no amount of electrolysis will produce any oxide (see also Foerster and Piguet's result quoted above); but if the nickel is allowed to lie in the liquid for 10–15 minutes without being connected *in* the circuit, and then the current is turned on, a heavy coat of black oxide will form on the metal immediately. I have ascertained by trial that no such coat of oxide appears unless the nickel has remained in the liquid

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[1] Even in the lead accumulator the transformations take place only through the liquid phase—at least, that is the most logical consideration. See Dolezalek: "Theory of Lead Accumulator."

[2] Naturally this will occur first in the liquid layer next to the anode.

for sometime *without* being anodically polarized, as a result of which it has regained its normal condition (shown by the potential), and hence when the circuit is closed some of the nickel is dissolved before the surface is "impaired" again. In accordance with this is the additional observation that a considerable quantity of oxide is readily formed when the current density is small, whereas no noticeable amount is formed if the current density is very large from the first. The direct oxidation of nickel is not noticeable in this connection.

Striking examples of *slow* oxidation at ordinary temperatures are at hand. Sproesser (20) found that carbon anodes, in the electrolysis of alkali chloride solutions, are oxidized very slightly although the oxygen discharged amounted to 30 per cent of the current used. Sackur (21) has shown that even hydrogen dissolved in and diffusing through dilute sulphuric acid to the anode is oxidized there very slowly. It appears that this state of affairs is rather general.

These experiments indicate that free oxygen may exist on a metal, and protect it in the same manner in which an oxide film would. An oxide may be formed, but its formation is incidental and of no consequence—unless a nonconducting oxide is formed extensively.[1]

If the conditions are such that an oxide with the requisite properties for passivity may be formed, it will appear without disturbing or changing the effect.

[1] It is a particular advantage of the view set forth above that it permits of a simple correlation of anode affects, including "valve action." Such correlation has become possible through two conclusions which can be drawn from the results obtained: (1) That "valve action" of anodes is due primarily to a layer of oxygen gas whose thickness depends upon the thickness of the "oxide skeleton" in which it is embedded (23). (2) That the same metal—*e. g.*, copper (16) and (24), zinc (11) and (23), magnesium (25) and (23)—when acting as an anode, under conditions that remain the same except as regards (*a*) solubility product of oxide and (*b*) anodic potential, may show either normal behavior, passivity, or valve action. As long as the ratio of current density to ionization velocity is not excessive, normal action will be shown. If this ratio is exceeded—either by increasing the current density or decreasing the active surface by precipitation of an oxide, then oxygen will also be discharged, giving rise to passivity phenomena. If an oxide is formed (usually by precipitation) and it is a "conducting" oxide, the anodic polarization remains low, as it is in passivity phenomena and in ordinary polarization on platinum. If the oxide is nonconducting the polarization rises very high—valve effect. Thus, with large current densities a copper anode in copper sulphate solution gives valve action; with moderate current densities, normal anodic behavior; also, in a slightly alkaline solution, with moderate current densities, it gives normal behavior; while with greater current densities or greater concentration of alkali, it gives the passivity effects observed by Erich Mueller.

It is evident that the idea of a "free oxygen cover"[1] has a decided advantage over the "special oxide cover," inasmuch as the conditions for its existence are not as limited as they are for the *special* oxide. But there is no fact which establishes one theory over the other.

This survey of the results obtained in the study of passivity shows us that the effect of the discharged oxygen will be to form an oxide or oxygen gas film which will protect or separate the anode area thus covered from the electrolyte. These areas will be referred to as *oxygen* or oxide spots without any intention of discriminating, because there are no indications in my results incompatible with either idea.

In the behavior of the nickel anode with larger current densities—with which both direct ionization of the metal and discharge of oxygen occur—the following facts require consideration:

(*a*) The lessening of the "active" surface with continued electrolysis.

(*b*) The "quasi" equilibrium conditions with the same current density at different potentials.

(*c*) The lower potentials shown after the current is interrupted—particularly the "air potential."

(*d*) The relation between the rate at which the surface is impaired and the concentration of hydroxyl ions.

(*e*) The relation between the rate of return to higher potentials and the concentration of hydrogen ions.

With the application of larger current densities than those already considered, the discharge of oxygen upon the electrode sets in because the discharge upon an electrode free from oxygen or oxide takes place very easily, and the electrostatic attraction between the pole and the liquid will be great enough. The lessening of the active surface with electrolysis indicates that the discharge of oxygen takes place upon separate spots, rather than uniformly all over the surface. This oxygen may remain as such or it may form an oxide—this is immaterial for the present. The uncovered "active" surface continues

[1] This is only a part of Fredenhagen's theory, and should not be mistaken for the whole.

its activity in sending out ions, and this activity becomes greater as the pole is farther from the point of equilibrium. The *oxygen* or *oxide* spots also exert their tendency to reionize: thus they may prevent partly or wholly the discharge of more oxygen. Two different areas of active surface occurring at different times on the same anode may be so related in distance from the equilibrium potential that they ionize at the same rate and thus support the same current density: this, together with no action on the oxygen spots—as just stated—may be the "quasi" equilibrium conditions. As the current densities are increased the active spots will become smaller and smaller in area. The oxygen may experience something similar to supersaturation, and when such a system "breaks" up, the oxygen spots may encroach *suddenly* upon the active area. This would be the case particularly when large current densities are required, and thus may come about the *sudden* "passivizing" drop often observed. When the current is interrupted, the active spots would not in general show the maximum potential immediately—as would be the case with an anode made up of different metals—instead, the oxygen spots also would begin to ionize, and the two kinds of area would act as a short-circuited cell—the active spots would show a potential depending upon the relative extent of the areas and the concentration in the oxygen spots. This latter will decrease rapidly until its own concentration is in equilibrium with the concentration of the oxygen dissolved in the electrolyte, when it will be "fed" by this, and the potential will remain at this point until the oxygen in the adjacent portions of the liquid is used up.

The observed effect due to a change of acidity or alkalinity in the electrolyte needs very little explanation, because it is plain that the discharge of oxygen out of an alkaline solution will take place more readily—and until the discharged oxygen has attained a greater concentration—than with a neutral solution, and the return to higher potentials will be slower with alkaline than with a neutral solution because the potential of the discharged oxygen in contact with an alkaline solution is less than when in contact with a neutral solution. Thus

the electromotive force of the cell (oxygen spot-electrolyte-active spot) will be less and hence the rate of change will be slower.

This explanation implies that a variation in the concentration of hydrogen ions does not affect the ionization velocity of the metal. That the latter is probably true is indicated by the following results: The polarization curve for $N/1$ nickel chloride solution (see Curve II.) is not particularly affected when the solution is acidified (see Curve VII.), whereas the polarization curve for $N/1$ nickel sulphate solution acidified to a corresponding degree is shifted until it falls even beyond Curve VII. (see Curve VI.). Had the variation of the concentration of hydrogen ions affected the ionization velocity of the nickel, then the curve for $N/1$ nickel chloride solution should have shifted to the right when the solution was acidified.

Finally it may be mentioned that the effect obtained with chloride solutions is considered to be due to the fact that a layer of oxygen is readily attacked by discharged chlorine, and converted to hypochlorite, etc. Thus the impairing of the surface by discharged oxygen is prevented and the current density that the surface can bear is greater. It is also considered that any discharged chlorine reacts quickly upon the metal, in contradistinction to oxygen.

Summary.

1. Nickel has a very small ionization velocity.

2. Most anodic current densities are in excess of the ionization velocity and hence result in the deposition of oxygen. A nickel anode covered with oxygen shows lower potentials than 0.48 volt.

3. The phenomena exhibited by *passive* nickel were studied and the theoretical relation of the ionization velocity and of the deposition of oxygen in these phenomena was pointed out.

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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 20°.[1]

By H. N. Morse and W. W. Holland.

The present series of 27 measurements of osmotic pressure was carried through without loss of concentration in any of the solutions while in the cells. After their removal from the cells they were all found to exhibit precisely the same rotation as other portions of the original solutions which had been reserved for polariscopic comparison at the conclusion of the experiments. In several of the more recent series of measurements, we had been able to avoid any sensible dilution in the lower concentrations of solution, but not in the higher ones. That we are now able to suppress all dilution of the cell contents is due to recent improvements in the cells which make it practicable to fill and close, and to open and empty them, so quickly that the solutions suffer no detectable dilution by water which is acquired from the porous walls. The abstraction of water from the cell walls, and, consequently, a dilution of the solution, occurs, of course, whenever the pressure upon

the latter is less than the maximum osmotic pressure. On this account, it was necessary to shorten greatly the time occupied in closing and opening the cells, and this has been reduced from 10 or 15 minutes to less than one minute by the improvements referred to, most of which were described in a former paper.[1]

The suppression of all dilution of the cell contents, whether weak or concentrated, is, without doubt, the most important single step forward which has been taken during our long continued endeavor to develop an accurate method for the measurement of osmotic pressure.

In this series (VIII.) at 20°, as in Series VII.[2] at 25°, there was no observable variation in bath temperature. This does not mean that the measurements are wholly free from *thermometer effects;* on the contrary, as will be seen in the records, most of them exhibit those slight fluctuations of pressure which we interpret as *thermometer effects* due to minute changes in the temperature of the solutions.

Unfortunately, the supply of the sugar with which the measurements at 10°, 15°, and 25° were made became exhausted before the series at 20° had been completed, and it was necessary to finish the work with other material. The sugar which was employed in the earlier work was a "rock candy," which, by analysis and by polariscopic examination, as well as by Fehling's test, was shown to be of exceptional purity. Hence no difficulty was anticipated in obtaining a new supply of suitable material of the same kind. But in this we were disappointed. Specimens of rock candy were procured from a number of different sources. All of them, however, were found to contain reducing sugars in such quantities as to render them unfit for our purpose. We then procured a quantity of "best" loaf sugar, and this was the material with which the series was completed. Its solutions gave very nearly the same rotations as those of the material which had previously been used, and the proportion of reducing sugar contained in it was—so far as we could determine by a series of comparative tests with Fehling's solution—less than one part in 1500. We

[1] This Journal, **40**, 266.
[2] *Ibid.*, **41**, 1.

shall, however, have occasion in the latter part of this paper to call attention to the fact that the osmotic pressure of its solutions was slightly higher than we had expected.

The results at 20° are given in this paper in the usual forms. Tables I.–XXVII. present the individual measurements in some detail. In Table XXVIII., the results are summarized for each experiment, and in Table XXIX., for each concentration of solution. Tables XXX. and XXXI. are introduced to show how the series of measurements at 20° compares with the earlier series at other temperatures in respect to osmotic pressure and the ratio of osmotic to gas pressure.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0 mm. Cell used, B_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 1.003; (2) liquids in manometer, 0.384; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.21. Time of setting up cell, 4 P.M., Dec. 14, 1908.

Time. Dec. 16.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
12.30 P.M.	20°.00	20°.00	122.44	2.523	2.39	0.133
5.00 P.M.	20°.00	19°.95	122.57	2.521	"	0.131
10.00 P.M.	20°.00	20°.10	122.20	2.530	"	0.140
Dec. 17.						
2.30 P.M.	20°.00	20°.00	122.47	2.526	"	0.136
				2.525	2.39	0.135

Molecular osmotic pressure, 25.55.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.056.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 20; volume of nitrogen, 409.01; displacement, 0 mm. Cell used, D_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 0.9974; (2) liquids in manometer, 0.44; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.51. Time of setting up cell, 4.00 P.M., Dec. 14, 1908.

Time. Dec. 17.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	20°.00	133.18	2.528	2.39	0.138
2.00 P.M.	20°.00	20°.00	133.73	2.518	"	0.128
9.00 P M.	20°.00	20°.00	133.81	2.519	"	0.129
Dec. 18.						
9.00 A.M.	20°.00	19°.80	134.57	2.512	"	0.122
				2.519	2.39	0.129

Molecular osmotic pressure, 25.19.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.054.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 24.95; (2) at conclusion of expr., 24°.95; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, F_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.90. Time of setting up cell, 3.30 P.M., Dec. 7, 1908.

Time. Dec. 8.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	19°.95	111.57	5.03	4.78	0.25
12.30 P.M.	20°.00	20°.10	111.55	5.03	"	0.25
9.00 P.M.	20°.00	20°.10	111.90	5.02	"	0.24
Dec. 9.						
10.30 A.M.	20°.00	20°.00	111.49	5.03	"	0.25
				5.03	4.78	0.25

Molecular osmotic pressure, 25.15.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.052.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 24°.95; (2) at conclusion of expr., 24°.95; loss, 0. *Manometer:* No. 20; volume of nitrogen, 409.01; displacement, 0. Cell used, G_3. Resistance of membrane, 170,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.52; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.34. Time of setting up cell, 3.30 P.M., Dec. 7, 1908.

Time. Dec. 7.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
10.00 P.M.	20°.00	20°.00	74.60	5.02	4.78	0.24
Dec. 9.						
10.00 A.M.	20°.00	20°.00	74.65	5.02	"	0.24
2.30 P.M.	20°.00	20°.00	74.62	5.02	"	0.24
				5.02	4.78	0.24

Molecular osmotic pressure, 25.10.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.050.

Table V.

0.2 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 24°.9; (2) at conclusion of expr., 24°.9; loss, 0. *Manometer:* No. 21; volume of nitrogen, 400.14; displacement, 0 mm. Cell used, G_3. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.56; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.86. Time of setting up cell, 4.00 P.M., Dec. 14, 1908.

Time. Dec. 15.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
10.00 P.M.	20°.00	20°.00	73.25	5.04	4.78	0.26
Dec. 16.						
9.00 A.M.	20°.00	20°.00	73.50	5.01	"	0.23
12.30 P.M.	20°.00	20°.00	73.52	5.02	"	0.24
10.00 P.M.	20°.00	20°.10	73.77	5.00	"	0.22
				5.02	4.78	0.24

Molecular osmotic pressure, 25.09.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.050.

Table VI.

0.3 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 36°.65; (2) at conclusion of expr., 36°.65; loss, o. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, o mm. Cell used, G$_8$. Resistance of membrane, 136,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.50; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 6.58. Time of setting up cell, 5.00 P.M., Nov. 27, 1908.

Time. Nov. 28.	Temperature.		Volume N$_2$.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	19°.90	48.02	7.45	7.17	0.28
2.00 P.M.	20°.00	20°.00	48.04	7.44	"	0.27
11.30 P.M.	20°.00	20°.00	48.03	7.45	"	0.28
Nov. 29.						
10.00 A.M.	20°.00	20°.00	48.08	7.44	"	0.27
				7.45	7.17	0.28

Molecular osmotic pressure, 24.82.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.038.

Table VII.

0.3 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 36°.65; (2) at conclusion of expr., 36°.65; loss, o. *Manometer:* No. 6; volume of nitrogen, 620.80; displacement, o. Cell used, C$_3$. Resistance of membrane, 250,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.50; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 6.82. Time of setting up cell, 4.00 P.M., Dec. 14, 1908.

Time. Dec. 15.	Temperature.		Volume N$_2$.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
5.00 P.M.	20°.00	20°.00	78.27	7.45	7.17	0.28
10.00 P.M.	20°.00	20°.00	78.25	7.45	"	0.28
Dec. 16.						
10.00 P.M.	20°.00	20°.10	78.12	7.46	"	0.29
Dec. 17.						
9.00 A.M.	20°.00	20°.00	78.17	7.45	"	0.28
				7.45	7.17	0.28

Molecular osmotic pressure, 24.84.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.038.

Table VIII.

0.4 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 48°.1; (2) at conclusion of expr., 48°.1; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, C_3. Resistance of membrane, 500,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.52; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.52. Time of setting up cell, 5.00 P.M., Nov. 7, 1908.

Time. Nov. 8.	Temperature.		Volume N_2	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.30 A.M.	20°.00	20°.00	36.66	9.96	9.56	0.40
10.00 P.M.	20°.00	20°.10	36.45	10.01	"	0.45
Nov. 9.						
9.00 A.M.	20°.00	20°.00	36.54	9.98	"	0.42
				9.98	9.56	0.42

Molecular osmotic pressure, 24.96.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.044.

Table IX.

0.4 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original 48°.15; (2) at conclusion of expr., 48°.15; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, G_3. Resistance of membrane, 225,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.52; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.57. Time of setting up cell, 5.00 P.M., Nov. 9, 1908.

Time. Nov. 10.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	20°.00	36.59	9.96	9.56	0.40
1.00 P.M.	20°.00	20°.00	36.66	9.94	"	0.38
5.00 P.M.	20°.20	20°.20	36.65	9.94	"	0.38
Nov. 11.						
9.00 A.M.	20°.00	20°.00	36.71	9.92	"	0.36
				9.94	9.56	0.38

Molecular osmotic pressure, 24.85.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.040.

Table X.

0.4 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 48°.0; (2) at conclusion of expr., 48°.0; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.80; displacement, 0. Cell used, F_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.51; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 3.00. Time of setting up cell, 4.00 P.M., Dec. 2, 1908.

Time. Dec. 3.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
5.00 P.M.	20°.00	20°.00	59.27	9.98	9.56	0.42
Dec. 4.						
9.00 A.M.	20°.00	20°.00	59.43	9.98	"	0.42
12.30 P.M.	20°.00	20°.00	59.60	9.95	"	0.39
4.00 P.M.	20°.00	20°.00	59.58	9.95	"	0.39
				9.97	9.56	0.41

Molecular osmotic pressure, 24.91.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.042.

Table XI.

0.5 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 58°.8; (2) at conclusion of expr., 58°.8; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0. Cell used, E_3. Resistance of membrane, 110,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.38. Time of setting up cell, 4.30 P.M., Nov. 2, 1908.

Time. Nov. 3.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
5.00 P.M.	20°.00	20°.20	32.31	12.48	11.95	0.53
11.30 P.M.	20°.00	20°.00	32.31	12.49	"	0.54
Nov. 4.						
8.30 A.M.	20°.00	20°.00	32.31	12.50	"	0.55
4.00 P.M.	20°.00	20°.00	32.34	12.49	"	0.54
				12.49	11.95	0.54

Molecular osmotic pressure, 24.98.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.045.

Table XII.

0.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 58°.7; (2) at conclusion of expr., 58°.7; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, F$_3$. Resistance of membrane, 272,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.74. Time of setting up cell, 5.00 P.M., Nov. 27, 1908.

Time.	Temperature.		Volume N$_2$.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Nov. 28.						
2.00 P.M.	20°.00	20°.00	34.71	12.48	11.95	0.53
11.30 P.M.	20°.00	20°.00	34.64	12.51	"	0.56
Nov. 29.						
10.00 A.M.	20°.00	20°.00	34.68	12.49	"	0.54
Nov. 30.						
9.00 A.M.	20°.00	20°.00	34.71	12.49	"	0.54
				12.49	11.95	0.54

Molecular osmotic pressure, 24.98.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.045.

Table XIII.

0.5 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 58°.9; (2) at conclusion of expr., 58°.9; loss, 0. *Manometer:* No. 21; volume of nitrogen, 400.14; displacement, 0. Cell used, C$_3$. Resistance of membrane, 182,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.84. Time of setting up cell, 4.00 P.M., Nov. 30, 1908.

Time.	Temperature.		Volume N$_2$.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Dec. 2.						
10.00 P.M.	20°.00	20°.00	31.09	12.50	11.95	0.55
Dec. 3.						
9.00 A.M.	20°.00	20°.00	31.09	12.49	"	0.56
11.00 A.M.	20°.00	20°.00	31.10	12.50	"	0.55
Dec. 4.						
4.00 P.M.	20°.00	20°.00	31.11	12.50	"	0.55
				12.50	11.95	0.55

Molecular osmotic pressure, 25.00.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.046.

Table XIV.

0.6 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 69°.4; (2) at conclusion of expr., 69°.4; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, C_3. Resistance of membrane, 500,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression 0.02. Initial pressure, 14.57. Time of setting up cell, 4.30 P.M., Nov. 3, 1908.

Time. Nov. 4.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 P.M.	20°.00	20°.20	24.41	15.15	14.34	0.81
Nov. 5.						
5.00 P.M.	20°.00	20°.20	24.38	15.17	"	0.83
9.00 P.M.	20°.00	20°.20	24.34	15.20	"	0.86
Nov. 6.						
8.30 A.M.	20°.00	20°.00	24.37	15.18	"	0.84
				15.18	14.34	0.84

Molecular osmotic pressure, 25.29.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.058.

Table XV.

0.6 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 69°.5; (2) at conclusion of expr., 69°.5; loss, 0. *Manometer:* No. 13; volume of nitrogen, 432.28; displacement, 0. Cell used, B_3. Resistance of membrane, 330,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.50. Time of setting up cell, 5.00 P.M., Nov. 4, 1908.

Time. Nov. 5.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	20°.00	27.73	15.22	14.34	0.88
12.30 P.M.	20°.00	20°.00	27.72	15.22	"	0.88
9.00 P.M.	20°.00	20°.00	27.72	15.22	"	0.88
Nov. 6.						
8.30 A.M.	20°.00	20°.00	27.75	15.21	"	0.87
				15.22	14.34	0.88

Molecular osmotic pressure, 25.36.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.061.

Table XVI.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 79°.4; (2) at conclusion of expr., 79°.4; loss, 0. *Manometer:* No. 13; volume of nitrogen, 432.33; displacement, 0. Cell used, A_3. Resistance of membrane, 225,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.71. Time of setting up cell, 3.00 P.M., Nov. 6, 1908.

Time. Nov. 7.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	20°.20	23.78	17.83	16.73	0.10
1.00 P.M.	20°.00	20°.00	23.78	17.83	"	0.10
4.30 P.M.	20°.00	20°.00	23.79	17.82	"	0.09
Nov. 8.						
9.30 A.M.	20°.00	20°.00	23.79	17.83	"	0.10
				17.83	16.73	0.10

Molecular osmotic pressure, 25.47.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.066.

Table XVII.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 79°.3; (2) at conclusion of expr., 79°.3; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, D_3. Resistance of membrane, 150,000. *Corrections:* (1) atmospheric pressure, 1.005; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.61. Time of setting up cell, 3.30 P.M., Dec. 8, 1908.

Time. Dec. 9.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	20°.00	24.53	17.83	16.73	1.10
2.00 P.M.	20°.00	20°.00	24.52	17.84	"	1.11
9.30 P.M.	20°.00	20°.00	24.48	17.86	"	1.13
Dec. 10.						
9.00 A.M.	20°.00	20°.00	24.49	17.85	"	1.12
				17.85	16.73	1.12

Molecular osmotic pressure, 25.49.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.067.

Table XVIII.

0.7 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 79°.3; (2) at conclusion of expr., 79°.3; loss, 0. *Manometer:* No. 21; volume of nitrogen, 400.14; displacement, 0. Cell used, F_3. Resistance of membrane, 275,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.63; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 16.66. Time of setting up cell, 4.00 P.M., Dec. 21, 1908.

Time. Dec. 22.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
1.00 P.M.	20°.00	20°.00	22.01	17.82	16.73	1.09
10.00 P.M.	20°.00	20°.00	22.01	17.83	"	1.10
Dec. 23.						
9.00 P.M.	20°.00	20°.10	22.00	17.83	"	1.10
12.30 P.M.	20°.00	20°.00	22.01	17.82	"	1.09
				17.83	16.73	1.10

Molecular osmotic pressure, 25.46.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.065.

Table XIX.

0.8 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 89°.25; (2) at conclusion of expr., 89°.25; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, A_3. Resistance of membrane, 162,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 20.36. Time of setting up cell, 4.00 P.M., Nov. 21, 1908.

Time. Nov. 21.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	20°.00	20°.20	18.13	20.58	19.12	1.46
Nov. 22.						
10.30 A.M.	20°.00	20°.00	18.07	20.64	"	1.52
Nov. 23.						
9.00 A.M.	20°.00	20°.10	18.09	20.62	"	1.50
12.30 P.M.	20°.00	19°.90	18.08	20.62	"	1.50
				20.62	19.12	1.50

Molecular osmotic pressure, 25.76.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.078.

Table XX.

0.8 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 89°.25; (2) at conclusion of expr., 89°.25; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, G_3. Resistance of membrane, 160,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 20.50. Time of setting up cell, 4.00 P.M., Dec. 2, 1908.

Time Dec. 3.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
8.00 P.M.	20°.00	20°.00	21.31	20.58	19.12	1.46
Dec. 4.						
9.00 A.M.	20°.00	20°.00	21.32	20.58	"	1.46
12.00 M.	20°.00	20°.00	21.35	20.55	"	1.43
4.00 P.M.	20°.00	20°.00	21.33	20.58	"	1.46
				20.57	19.12	1.45

Molecular osmotic pressure, 25.72.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.076.

Table XXI.

0.8 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 89°.15; (2) at conclusion of expr., 89°.15; loss, 0. *Manometer:* No. 22; volume of nitrogen, 416.14; displacement, 0. Cell used, C_3. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.59. Time of setting up cell, 4.00 P.M., Dec. 18, 1908.

Time. Dec. 19.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
8.30 P.M.	20°.00	20°.05	19.81	20.63	19.12	1.51
Dec. 20.						
8.30 P.M.	20°.00	19°.80	19.83	20.61	"	1.49
Dec. 21.						
1.00 P.M.	20°.00	20°.00	19.83	20.61	"	1.49
Dec. 22.						
9.00 A.M.	20°.00	20°.00	19.82	20.61	"	1.49
				20.62	19.12	1.50

Molecular osmotic pressure, 25.77.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.078.

Table XXII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 98°.5; (2) at conclusion of expr., 98°.5; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, D_3. Resistance of membrane, 157,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 22.77. Time of setting up cell, 2.30 P.M., Dec. 5, 1908.

Time. Dec. 6.	Temperature.		Volume N₂.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
3.00 P.M.	20°.00	20°.00	26.10	23.36	21.51	1.85
9.00 P.M.	20°.00	20°.00	26.10	23.37	"	1.86
Dec. 7.						
9.00 A.M.	20°.00	20°.00	26.12	23.36	"	1.85
2.30 P.M.	20°.00	20°.00	26.13	23.35	"	1.84
				23.36	21.51	1.85

Molecular osmotic pressure, 25.96.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.086.

Table XXIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 98°.3; (2) at conclusion of expr., 98°.3; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, F_3. Resistance of membrane, 550,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 19.92. Time of setting up cell, 4.00 P.M., Dec. 17, 1908.

Time. Dec. 18.	Temperature.		Volume N₂.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
12.30 P.M.	20°.00	20°.00	18.84	23.34	21.51	1.83
8.30 P.M.	20°.00	20°.00	18.85	23.32	"	1.81
Dec. 19.						
10.30 A.M.	20°.00	20°.00	18.87	23.28	"	1.77
2.00 P.M.	20°.00	20°.00	18.86	23.29	"	1.78
				23.31	21.51	1.80

Molecular osmotic pressure, 25.90.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.084.

Table XXIV.

0.9 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 98°.3; (2) at conclusion of expr., 98°.3; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, A₃. Resistance of membrane, 135,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 19.47. Time of setting up cell, 4.00 P.M., Dec. 17, 1908.

| Time. Dec. 18. | Temperature. | | Volume N₂. | Pressure. | | |
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	20°.00	19°.80	26.22	23.27	21.51	1.76
8.30 P.M.	20°.00	20°.00	26.22	23.27	"	1.76
Dec. 19.						
10.30 A.M.	20°.00	20°.00	26.21	23.27	"	1.76
2.00 P.M.	20°.00	20°.00	26.20	23.27	"	1.76
				23.27	21.51	1.76

Molecular osmotic pressure, 25.86.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.082.

Table XXV.

1.00 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 107°.45; (2) at conclusion of expr., 107°.45; loss, 0. *Manometer:* No. 22; volume of nitrogen, 416.14; displacement, 0. Cell used, B₃. Resistance of membrane, 300,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 25.60. Time of setting up cell, 4.00 P.M., Dec. 3, 1908.

| Time. Dec. 4. | Temperature. | | Volume N₂. | Pressure. | | |
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
12.30 P.M.	20°.00	20°.00	15.71	26.12	23.90	2.22
11.30 P.M.	20°.00	20°.00	15.72	26.10	"	2.20
Dec. 5.						
8.30 A.M.	20°.00	19°.95	15.72	26.10	"	2.20
1.00 P.M.	20°.00	20°.00	15.70	26.14	"	2.24
				26.12	23.90	2.22

Molecular osmotic pressure, 26.12.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.093.

Table XXVI.

1.00 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 107°.45; (2) at conclusion of expr., 107°.45; loss, o. *Manometer:* No. 20; volume of nitrogen, 409.01; displacement, o. Cell used, G_3. Resistance of membrane, 143,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.60; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 17.64. Time of setting up cell, 4.00 P.M., Dec. 18, 1908.

Time. Dec. 20.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
8.30 P.M.	20°.00	19°.80	15.44	26.12	23.90	2.22
Dec. 21.						
9.00 A.M.	20°.00	20°.00	15.43	26.13	"	2.23
5.00 P.M.	20°.00	20°.00	15.43	26.13	"	2.23
10.00 P.M.	20°.00	20°.00	15.42	26.14	"	2.24
				26.13	23.90	2.23

Molecular osmotic pressure, 26.13.

Molecular gas pressure, 23.90.

Ratio of osmotic to gas pressure, 1.093.

Table XXVII.

1.00 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 107°.4; (2) at conclusion of expr., 107°.4; loss, o. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, o. Cell used, B_3. Resistance of membrane, 183,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.57; (3) dilution, o; (4) concentration, o; (5) capillary depression, 0.02. Initial pressure, 24.27. Time of setting up cell, 4.00 P.M., Dec. 21, 1908.

Time. Dec. 22.	Temperature.		Volume N_2.	Pressure.		
	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
1.00 P.M.	20°.00	20°.00	23.40	26.11	23.90	2.21
10.30 P.M.	20°.00	20°.00	23.40	26.12	"	2.22
Dec. 23.						
9.00 A.M.	20°.00	20°.10	23.40	26.11	"	2.21
12.30 P.M.	20°.00	20°.00	23.40	26.11	"	2.21
				26.11	23.90	2.21

Molecular osmotic pressure, 26.11.

Molecular gas pressure, 23.90.

Ratio of osmotic to gas pressure, 1.093.

Table XXVIII.—*Summary of Results at 20°.*

Weight normal concentration.	Osmotic pressure.	Gas pressure.	Difference	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	2.525	2.39	0.135	25.25	23.90	1.056
"	2.519	"	0.129	25.19	"	1.054
0.2	5.03	4.78	0.25	25.15	"	1.052
"	5.02	"	0.24	25.10	"	1.051
"	5.02	"	0.24	25.09	"	1.050
0.3	7.45	7.17	0.28	24.82	"	1.038
"	7.45	"	0.28	24.84	"	1.038
0.4	9.98	9.56	0.42	24.96	"	1.044
"	9.94	"	0.38	24.85	"	1.040
"	9.97	"	0.41	24.91	"	1.042
0.5	12.49	11.95	0.54	24.98	"	1.045
"	12.49	"	0.54	24.98	"	1.045
"	12.50	"	0.55	25.00	"	1.046
0.6	15.18	14.34	0.84	25.29	"	1.058
"	15.22	"	0.88	25.36	"	1.061
0.7	17.83	16.73	1.10	25.47	"	1.066
"	17.85	"	1.12	25.49	"	1.067
"	17.83	"	1.10	25.46	"	1.065
0.8	20.62	19.12	1.50	25.76	"	1.078
"	20.57	"	1.45	25.72	"	1.076
"	20.62	"	1.50	25.77	"	1.078
0.9	23.36	21.51	1.85	25.96	"	1.086
"	23.31	"	1.80	25.90	"	1.084
"	23.27	"	1.76	25.86	"	1.082
1.0	26.12	23.90	2.22	26.12	"	1.093
"	26.13	"	2.23	26.13	"	1.093
"	26.11	"	2.21	26.11	"	1.093

Table XXIX.—*Summary of Results at 20°.   Mean Values.*

Weight normal concentration.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	2.522	2.39	0.132	25.22	23.90	1.055
0.2	5.023	4.78	0.243	25.11	"	1.051
0.3	7.45	7.17	0.28	24.83	"	1.038
0.4	9.96	9.56	0.40	24.91	"	1.042
0.5	12.49	11.95	0.54	24.99	"	1.045
0.6	15.20	14.34	0.86	25.33	"	1.060
0.7	17.84	16.73	1.11	25.47	"	1.066
0.8	20.60	19.12	1.48	25.75	"	1.077
0.9	23.31	21.51	1.80	25.91	"	1.084
1.0	26.12	23.90	2.22	26.12	"	1.093

Table XXX.—Osmotic Pressures.   Series III.–VIII.

Weight normal concentration.	Series III. Pressures. 0°.	Series IV. Pressures. 4°-5°.	Series V. Pressures. 10°.	Series VI. Pressures. 15°.	Series VIII. Pressures. 20°.	Series VII. Pressures. 25°.
0.1	2.42	2.40	2.44	2.48	2.52	2.56
0.2	4.79	4.75	4.82	4.91	5.02	5.10
0.3	7.11	7.07	7.19	7.33	7.45	7.57
0.4	9.35	9.43	9.58	9.78	9.96	10.12
0.5	11.75	11.82	12.00	12.29	12.49	12.73
0.6	14.12	14.43	14.54	14.86	15.20	15.42
0.7	16.68	16.79	17.09	17.39	17.84	18.02
0.8	19.15	19.31	19.75	20.09	20.60	20.73
0.9	21.89	22.15	22.28	22.94	23.31	23.66
1.0	24.45	24.53	25.06	25.42	26.12	26.33
1. Total pressure	131.71	132.68	134.75	137.49	140.52	142.24
2. Mean ratio of osmotic to gas pressure	1.074	1.065	1.061	1.064	1.069	1.064
3. Mean loss in rotation (per cent)	1.73	1.45	0.22	0.10	0.00	0.20

Table XXXI.—Mean Ratios of Osmotic to Gas Pressures.
Sereis III.—VIII.

Weight normal concentration.	Series III. Ratios. 0°.	Series IV. Ratios. 4°–5°.	Series V. Ratios. 10°.	Series VI. Ratios. 15°.
0.1	1.085	1.060	1.056	1.053
0.2	1.074	1.045	1.043	1.045
0.3	1.064	1.041	1.038	1.040
0.4	1.049	1.042	1.037	1.040
0.5	1.055	1.043	1.040	1.046
0.6	1.056	1.059	1.050	1.055
0.7	1.070	1.060	1.058	1.058
0.8	1.074	1.067	1.069	1.069
0.9	1.091	1.081	1.073	1.085
1.0	1.097	1.084	1.085	1.083

Weight normal concentration.	Series VIII. Ratios. 20°.	Series VII. Ratios. 25°.	Series V.–VIII. Mean ratios.	
0.1	1.055	1.053	1.054	. . . . .
0.2	1.051	1.048	1.047	. . . . .
0.3	1.038	1.038	1.039	. . . . .
0.4	1.042	1.041	1.040	. . . . .
0.5	1.045	1.048	1.045	. . . . .
0.6	1.060	1.058	1.056	. . . . .
0.7	1.066	1.059	1.060	. . . . .
0.8	1.077	1.066	1.070	. . . . .
0.9	1.084	1.082	1.081	. . . . .
1.0	1.093	1.084	1.086	. . . . .

If Table XXX. is examined, it will be seen (horizontal line No. 1) that the aggregate pressure of Series VIII. at 20° is 140.52 atmospheres, while those of Series VI. at 15° and of Series VII. at 25° are 137.49 and 142.24 atmospheres, respectively. The total pressure which would have been expected for Series VIII.—if the temperature coefficient of osmotic pressure is equal to that of gases—is about 139.87 atmospheres. In other words, the series, considered as a unit, gave a pressure greater by 0.65 atmosphere than is consistent with its temperature relation to Series VI. at 15° and Series VII. at 25°. The same fact is brought out still more clearly by the ratios of osmotic to gas pressures given in horizontal line No. 2 (Table XXX.). It will there be seen that this ratio for Series VI. at 15°, and for Series VII. at 25°, is 1.084; while for Series

VIII. at 20°, it is 1.089, *i. e.*, one-half per cent higher than would have been expected if osmotic pressure obeys the law of Gay-Lussac for gases. We do not permit ourselves as yet to entertain any "*views*" regarding the proper magnitude of osmotic pressure at any temperature; nevertheless, we are prepared to state that all the best experimental evidence which we are securing is tending strongly in the direction of establishing the substantial equivalence of the temperature coefficients of osmotic and gas pressures, and that the major portion of the discrepancy, to which attention has been drawn, is easily explained without calling this equivalence into question. It was noted that, as long as the old supply of sugar was employed, the ratios of osmotic to gas pressure at 20° agreed well with those which had been found at 15° and 25°, but that these ratios increased as soon as the new material was brought into use. It would seem, therefore, that the difference in question was due, in large part, to the impurities of the new material. It was noted, also, that the increase in the ratio of osmotic to gas pressure which followed the introduction of the new supply of sugar was, as a rule, relatively greater in the higher concentrations of solution, *i. e.*, in those concentrations which, in all the earlier work, had suffered some dilution while in the cells. The meaning of the latter observation is clear. It signifies that the ratios hitherto obtained are probably somewhat too low in those cases in which dilution of the cell contents occurred.

THE ABSORPTION SPECTRA OF SOLUTIONS OF A NUMBER OF SALTS IN WATER, IN CERTAIN NONAQUEOUS SOLVENTS, AND IN MIXTURES OF THESE SOLVENTS.

[TWENTY-FOURTH COMMUNICATION.]

BY HARRY C. JONES AND JOHN A. ANDERSON.

[Continued from March Number.]

SALTS OF NEODYMIUM, PRASEODYMIUM, AND ERBIUM.

Some of the more important investigations on the salts of the above-named elements are the following:

Bahr and Bunsen[1] included didymium and erbium in their early work on absorption spectra.

Becquerel,[2] in his study of spectra in the infrared region, worked with didymium. In his subseqeunt work[3] on the variation of absorption spectra in crystals, the sulphate and nitrate of didymium were included.

Becquerel[4] compared the absorption spectra of crystals of didymium salts with the spectra of the aqueous solution of the same salts. He showed that from the displacement of the bands he could recognize distinct substances or definite compounds, and that in the crystals we may have, simultaneously, mixtures of different compounds and especially basic salts.

Demarcay[5] studied the spectrum of didymium, and concluded that in addition to praseodymium and neodymium a third element was probably present. In a subsequent investigation[6] he shows that neodymium from entirely different minerals and sources always has the same spectrum, and concludes that it is a chemical element.

Krüss and Wilson[7] carried out an elaborate investigation on the absorption spectra of the rare earths. They concluded that we must assume the existence of more than twenty elements in the various rare earth minerals.

Bettendorff[8] carried out three investigations on the spectra of the cerium and yttrium group, and Schottländer[9] made use of his spectroscopic studies and spectrophotometric work to characterize the various rare earths.

Boudouard[10] effected the separation of neodymium and praseodymium by means of potassium sulphate instead of ammonium nitrate. The absorption spectra indicated that the separation was nearly complete.

[1] Ann. Chem. (Liebig), **137**, 1 (1886).
[2] Ann. Chim. Phys. [5], **30**, 5 (1883).
[3] *Ibid.* [6], **14**, 170 (1888).
[4] *Ibid.*, [6], **14**, 257 (1888).
[5] Compt. rend., **102**, 1551 (1886); **105**, 276 (1887).
[6] *Ibid.*, **126**, 1040 (1898).
[7] Ber. d. chem. Ges., **20**, 2134 (1887).
[8] Ann. Chem. (Liebig), **256**, 159 (1890); **263**, 164 (1891); **270**, 376 (1892).
[9] Ber. d. chem. Ges., **25**, 569 (1892).
[10] Compt. rend., **126**, 900 (1898).

Scheele[1] did some very careful work on praseodymium in connection with his determination of the atomic weight of that element, and later[2] in connection with the separation of praseodymium and neodymium.

The elaborate investigations of Muthmann[3] and his co-workers, Stützel, Böhm, Baur, Hofer, and Weiss, call for special comment. These authors raise the question as to the elementary nature of praseodymium and neodymium, and point out certain lines of evidence, based on spectrum analysis, which make it not impossible that these substances are mixtures. They show that by spectrum analysis it is possible to determine approximately the amounts of neodymium and praseodymium in a mixture of the two, a fact which had earlier been utilized by Jones[4] in his work on the atomic weights of these two elements.

By the electrolysis of fused neodymium compounds Muthmann was able to prepare the pure metal. He then studied the physical properties not only of neodymium, but also of cerium, lanthanum, and praseodymium, which were prepared in the same manner.

An important and interesting investigation was carried out by Liveing[5] on the effects of dilution, temperature, nature of the solvent, etc., on the absorption spectra of solutions of didymium and erbium salts. His eye observations were made with an ordinary spectroscope, and the photographs also with a prism spectroscope. He obtained some very good plates, indeed, considering the kind of apparatus employed. He studied the effect on the absorption of increasing the dilution of the solution, and established the four following facts:

The spectra of the different salts of the same metal in dilute solution are identical. The spectrum is constant for the chloride and sulphate in different dilutions, as long as the thickness of the absorbing solutions is proportional to the

[1] Z. anorg. Chem., **17,** 310 (1898).

[2] Ber. d. chem. Ges., **32,** 409 (1899).

[3] Ber. d. chem. Ges., **32,** 2653 (1899); **33,** 42, 1748, 2028 (1900); Ann. Chem. (Liebig), **320,** 231 (1902).

[4] This Journal, **20,** 345 (1898).

[5] Camb. Phil. Soc., **18,** 298 (1900).

dilution. The spectrum of the nitrate is modified by some cause with increasing concentration.

The absorption of the short wave lengths, which differs for different salts, diminishes with increased dilution. Rise in temperature from about 20° to 97° renders the bands more diffuse, but does not increase their intensity. The addition of acid made the absorption in general more diffuse, but did not weaken the absorption.

From these facts Liveing concluded that absorption cannot be accounted for on the basis of electrolytic dissociation.

His work on absorption in nonaqueous solvents is of special interest in the present connection.

He states that didymium chloride dried at a temperature above 100° is quite insoluble in alcohol. This was doubtless due to the formation of the basic chloride. This salt can be heated to 140° to 150° in a current of dry hydrochloric acid gas, and the anhydrous salt is still completely soluble in alcohol. The salt with which he worked doubtless contained more or less water.

He says, further, that the absorption spectrum of the alcoholic solution shows the same bands as that of an aqueous solution, but they are somewhat modified. The positions of maximum absorption are all moved towards the red. The shift of the different bands is not equal. The bands in the yellow and green in the alcoholic solution are so shifted as to suggest the appearance of new bands, but Liveing states that by studying solutions of different concentrations he has convinced himself that no new bands appear. We shall see that this is an error.

He found that glycerol produced the same changes as alcohol in the spectrum of aqueous solutions. He closes thus: [1]

"On a review of the whole series of observations, I conclude that the characteristic absorption of didymium compounds, namely, those which are common to dilute aqueous solutions, and are only modified by concentration, by heat, and by variations of the solvent, are due to molecules which are iden-

[1] Camb. Phil. Soc., **18**, 314 (1900).

tical in all cases, though their vibrations are modified by their relations to other molecules surrounding them."

Urbain[1] devised a new method for separating the rare earths, using ethyl sulphate.

Drossbach,[2] in his work on absorption in the region of the ultraviolet, measured a number of the bands of praseodymium and neodymium; and Hartley[3] included the nitrate of erbium in his investigation on the absorption spectra of metallic nitrates. In the discussion of his results, Hartley calls attention to the fact that Bunsen[4] found that didymium salts in the crystallized state and in solution show absorption bands that vary in width with the thickness of the absorbing medium and with the quantity of the salt. Solutions of the chloride, sulphate, and acetate, each containing the same weight of didymium, yielded different spectra, the bands being shifted towards the red end of the spectrum with increase in the molecular weight of the salt.

Hartley points out that more recently Becquerel[5] observed similar variation in the absorption spectra, both in crystals and in solutions; while Muthmann and Stützel[6] found marked differences between the spectra of solutions of the different salts of neodymium, such as the chloride, nitrate, and carbonate.

As Hartley points out, these facts cannot be reconciled with the theory that the absorption spectra of solutions of neodymium salts are due to the neodymium ion, since the solutions of the above-named salts contain, for comparable concentrations, practically the same number of neodymium ions. He then concludes his paper with the paragraph already quoted. Among the more recent investigations on the salts of the rare earths is that of Miss Helen Schaeffer.[7] She attempted to test Kundt's law for the nitrates of certain rare earths, such as neodymium and cerium. She employed the

[1] Compt. rend., **126**, 835; **127**, 107 (1898).
[2] Ber. d. chem. Ges., **35**, 1486 (1902); Ann. Chim. Phys. [7], **19**, 184 (1900).
[3] J. Chem. Soc., **83**, 221 (1903).
[4] Pogg. Ann., **128**, 100 (1866).
[5] Compt. rend., **104**, 777, 1691 (1887).
[6] Ber. d. chem. Ges., **32**, 2653 (1899).
[7] Physik. Z., **7**, 822 (1906).

following solvents: Water, methyl alcohol, ethyl alcohol, propyl alcohol, isobutyl alcohol, amyl alcohol, allyl alcohol, glycerol, and acetone. Solutions containing 1 gram of the salt in 10 cc. of the solvent were used. She found that, in general, the bands had a different arrangement in the various solvents, and in order to identify the bands she worked with mixtures of the various solvents, so as to get what she supposed was a gradual shift of the bands. Her plates, however, show that instead of having a shift in the bands, she had two sets of bands existing simultaneously.

In the second part of her investigation she studied change in absorption with change in concentration; in other words, whether Beer's law held. She found that with decreasing concentration there is a shift in the yellow band towards the violet. The most concentrated solutions with which she worked contained about 30.5 grams of didymium nitrate in 10 cc. water. She concludes that all of the facts established by her investigation can be accounted for in terms of electrolytic dissociation alone.

An excellent piece of work on the absorption spectra of aqueous solutions of neodymium chloride has recently been done by Rech.[1] The absorption bands were carefully measured as far down into the red as the sensibility of his plates would permit. There is transmission farther down into the red than could be detected by the plates which he employed.

The absorption spectra of a number of the powdered salts of neodymium and erbium were recently studied by Anderson.[2] These included the chloride, nitrate, sulphate, and oxalate. He found that each salt has its own definite absorption, which is different from that shown by any other salt.

Preparation of Anhydrous Salts.

In working in nonaqueous solvents, it is, of course, necessary to have the dissolved salts perfectly anhydrous. A number of the salts used in this investigation cannot be dried in the air by simply raising the temperature. Under these

[1] Dissertation, Bonn, 1906.
[2] Astro-Phys. Rev., **26**, 73 (1907).

conditions the oxy salt would be formed. This applies to most of the chlorides and bromides whose nonaqueous solutions were studied in this work.

In every such case the chloride in question was dried in a current of dry hydrochloric acid gas. It was placed in a porcelain boat, which was then inserted into a glass tube through which the current of dry hydrochloric acid gas was passed. The glass tube was then heated in an air bath to the temperature required to remove all of the water from the salt.

In removing all of the water from a bromide, the salt was treated in every respect like the chloride, except that it was dried in a current of dry hydrobromic acid gas. The usual methods of testing the purity of all of the compounds employed, and of standardizing the mother solutions of these substances, were used. A detailed discussion of this subject would be superfluous.

The praseodymium and neodymium, in the form of the double nitrate with ammonium, were furnished us by the Welsbach Light Company, with their characteristic generosity, and it gives us unusual pleasure to express here our heartiest thanks to their chemist, Dr. H. S. Miner. The chemists of this company have always shown a spirit of coöperation with scientific work on the rare elements that is very unusual, and for which men of science, working in this field, owe them a lasting debt of gratitude.

The praseodymium used in this work was practically free from neodymium, containing only a few hundredths of 1 per cent of that element. From the spectrograms it would appear that the neodymium used contained about 6 per cent of praseodymium. The erbium, of course, contained quite a considerable amount of impurities.

A number of the salts of neodymium, praseodymium, and erbium were studied thoroughly in the present connection, and yielded some of the most interesting and important results obtained in this investigation.

Thus, plates were prepared for: Neodymium chloride in water—Beer's law; neodymium chloride in water—molecules constant; neodymium chloride in water with calcium chloride

and with aluminium chloride; neodymium chloride in methyl alcohol—Beer's law; neodymium chloride in ethyl alcohol—Beer's law; neodymium chloride in mixtures of methyl alcohol and water; neodymium chloride in ethyl alcohol to which water is added; neodymium chloride —anhydrous; neodymium bromide in water—Beer's law; neodymium nitrate in water—Beer's law; neodymium nitrate in water—molecules constant; neodymium nitrate in methyl alcohol—Beer's law; neodymium nitrate in ethyl alcohol—Beer's law; neodymium nitrate in acetone—Beer's law; neodymium nitrate in mixtures of methyl alcohol and water; neodymium nitrate in mixtures of acetone and water; praseodymium chloride in water—Beer's law; praseodymium chloride in mixtures of the alcohols and water; praseodymium nitrate in water—Beer's law; erbium chloride in water—Beer's law; erbium nitrate in water—Beer's law.

On account of the relative importance of the results in this section of our work, fifteen plates for the salts of the rare earths are given.

Neodymium Chloride in Water—Beer's Law (See Plates XI. and XII.).

Five different sets of solutions, covering as wide a range of concentrations as possible, were made up, the object being not only to test Beer's law thoroughly, but also to get as complete a map as possible of the absorption spectrum of neodymium chloride. In very concentrated solutions a certain group of bands may appear as a single band, due to the widening of the individual band or to general absorption in the region considered. By diminishing the concentration such a "band" breaks up gradually into its components, and hence to map completely the absorption spectrum it is necessary to work over a wide range of concentrations.

If the object were simply to "map the spectrum" this could, of course, be most conveniently done by keeping the depth of layer constant and changing the concentration through a sufficient range, thus getting the complete spectrum on a single film; but since the chief object here was to test Beer's

law it was necessary to make several sets of solutions covering different regions of concentration. The concentrations of the solutions used in making the negative for A, Plate XI., beginning with the one whose spectrum is adjacent to the numbered scale, were 3.40, 3.02, 2.72, 2.38, 2.17, 1.90, and 1.70; the corresponding depths of cell were 12, 13.5, 15, 17, 19, 21.5, and 24 mm. For B, Plate XI., the concentrations were 3.40, 2.55, 1.70, 1.13, 0.80, 0.57, and 0.43; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For A, Plate XII., the concentrations were 1.70, 1.27, 0.85, 0.57, 0.40, 0.28, and 0.22; for B, Plate XII., they were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14, and 0.11. The depths of absorbing layer were in each case the same as in B, Plate XI. It will be noticed that beginning with B, Plate XI., the concentrations used in each succeeding set are just halved each time.

The most concentrated solutions appeared brownish-yellow in their bottles, and changed on dilution to a yellowish-pink, the color being extremely faint in the most dilute solutions.

The exposures to the light of the Nernst lamp and spark were 1 and 2 minutes, respectively, the slit having a width of 0.01 cm. The exposures and slit width were not varied in the work recorded in the present section, the object being to make the spectrograms as nearly comparable as possible.

Both A and B, of Plate XI., show the presence of some general absorption in the ultraviolet, which decreases quite rapidly with dilution. The absorption bands also narrow somewhat with decrease in concentration, especially from 3.4 normal to about 1.7 normal. For concentrations less than about 1.5 normal Beer's law seems to hold very accurately indeed, with the exception of the shading towards the red accompanying the band near λ 5800, which seems to decrease somewhat with dilution for concentrations of normal or less.

In the following table the measurements of the positions of the bands were made on the seventh strip of A, Plate XI., and refer, therefore, to a concentration of 1.7 normal with a

Plate XI.
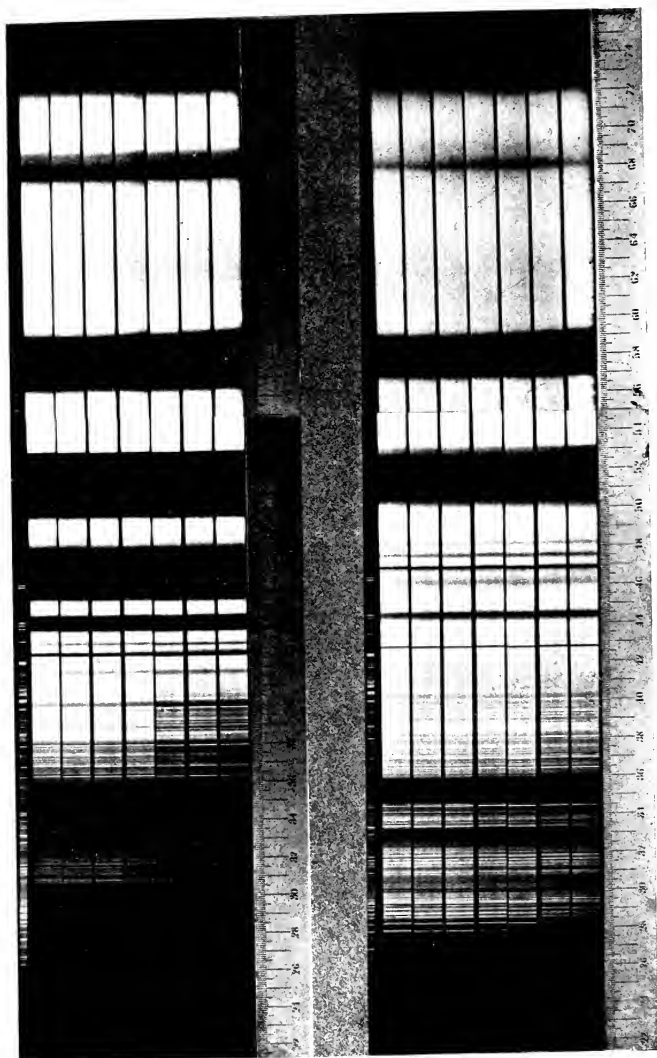
A

B

depth of layer of 24 mm. The remarks referring to changes with dilution apply to a change in concentration from 3.4 to 1.7 normal, the depths of layer being so varied that the product of concentration and depth remains constant.

λ.	Character.	Remarks.
2810	Faint transmission begins	
2890–2910	Band with well-defined sharp edges	
2970–2995	A double band, strongest component to violet	The observed narrowing with dilution perhaps due largely to general U.V. absorption
3220–3330	Strong band of complete absorption, sharp edges	Narrows slightly with dilution
3380–3400	Rather faint band. Most intense towards red	
3435–3595	Complete absorption. Edges sharp	
4180	Hazy, not very intense	Narrows somewhat with dilution
4275	Very intense and sharp	Narrows considerably at first
4290	Narrow and faint	Between this and λ 4275 there is fairly strong absorption in the most concentrated solution. This absorption has disappeared in the spectrum measured
4330	Hazy	
4410–4465	Edges rather hazy	This band is coincident with band due to praseodymium, and is to be ascribed to this element, which had not been completely separated from the neodymium. It does not change with dilution
4580–4650	Band with hazy edges, not completely separated from 4665–4710	Narrows slightly with dilution
4665–4710	More sharply defined on red than on violet side	Partly due to praseodymium Does not change with dilution

λ.	Character.	Remarks.
4740–4770	Fairly sharp edges	Not affected by dilution
4820	Hazy on violet side	Due at least partly to **praseodymium**
5000–5330	Red limit sharp, violet a little hazy	Violet shading a little **greater** in concentrated solutions
5660–5930	Violet limit sharp. Red edge hazy	Shading on red side decreases with dilution
6235	First and strongest band in orange group	Not affected by dilution
6260	Narrow and rather faint	"
6270–6310	Faint band	"
6300–6390	"	"
6730	Faint. In shading of principal red band	"
6770–6840	Principal red band. Edges hazy	"
6890	Band with hazy edges	"
7250	End of transmission	"

The most marked change produced by dilution from 3.4 to 1.7 normal, excepting that in the red shading of the λ 5660 to λ 5930 band, is that which takes place on the red side of the narrow absorption line at λ 4275. In the spectrum of the most concentrated solution the red edge of this line falls at λ 4280, from which a uniform absorption extends to λ 4295. In the third spectrum, counting from the numbered scale, the shading has almost completely disappeared, leaving a very narrow line at approximately λ 4290. The width of this line is only 2 or 3 A.U., and it persists with unchanged intensity throughout the remaining strips of the spectrogram. Its intensity is, however, not sufficient to make it show in the reproduction, and not even great enough to make it visible on the negative for B, Plate XI.

The limits of transmission for the yellow band, as shown by the spectrum of the most concentrated solution, are λ 5660 and λ 5950; hence the narrowing of its red side amounts to 20 A.U.

B, Plate XI., starts at the same concentration as A, but the effective depth of absorbing layer is only one-fourth of

Plate XII.
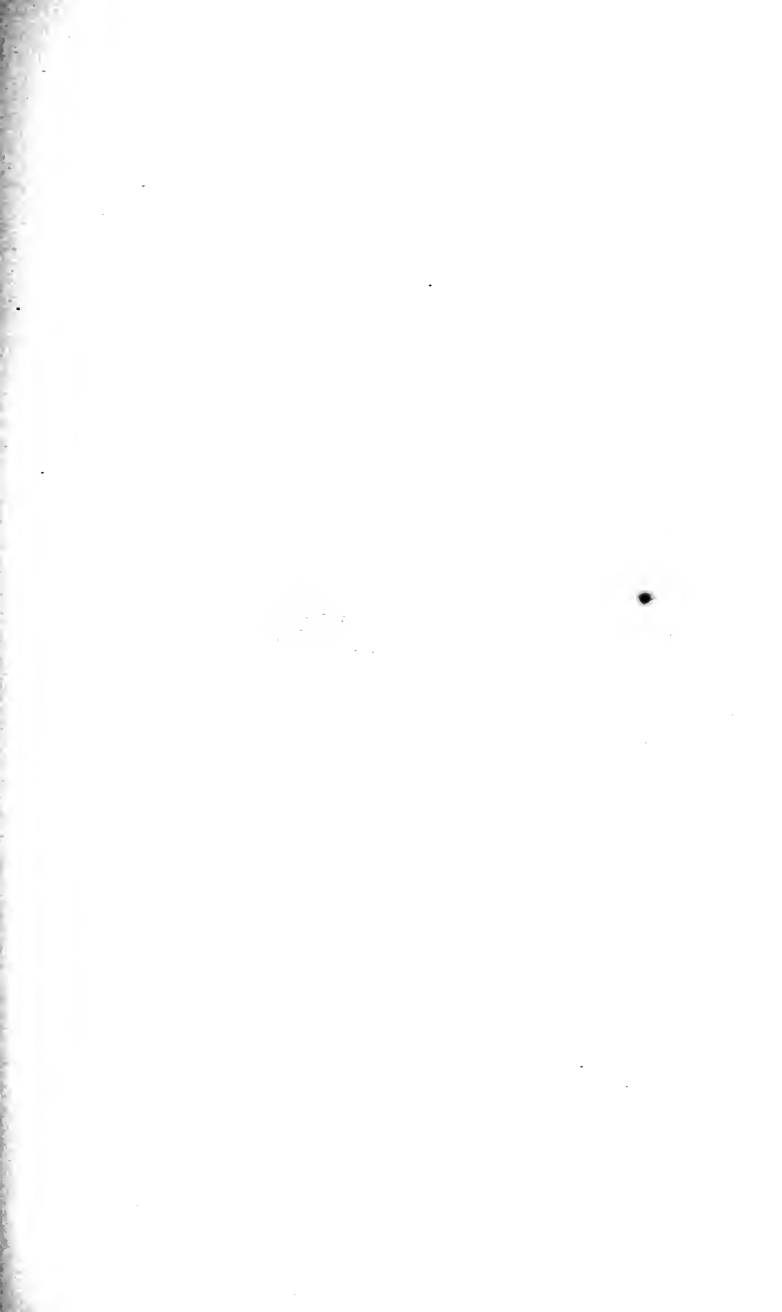
A.

B.

that used in A. Hence this spectrogram represents the spectrum of a solution of neodymium chloride 24 mm. deep and having a concentration of 0.43 normal. The absorption bands are all much narrower, and several of them are shown in the process of breaking up into simpler bands. The bands in the ultraviolet have disappeared, excepting the one at λ 3435 to λ 3595, which is still intense, and a trace of the one at λ 3220 to λ 3330. Transmission in this region now extends faintly to λ 2460. No new absorption bands beyond λ 2800 can be seen.

The λ 3435 to λ 3595 band now has the limits λ 3450 to λ 3580, and shows a weak transmission at λ 3485, which increases somewhat with dilution, the band thus being divided into two. In A, Plate XII., this has broken up further into bands having their centers at λ 3465, λ 3500, λ 3540, and λ 3560, the bands at λ 3465 and λ 3540 being the narrowest and most intense. In B, Plate XII., λ 3465 and λ 3540 are both narrow, intense bands, while λ 3500 is faint and wide; λ 3560 has disappeared entirely as a band.

The band at λ 4180 is weak throughout B, Plate XI., and may be said to have disappeared in A, Plate XII. The narrow band at λ 4275 is very persistent. Its width remains about the same as that shown by the negative for B, Plate XI., throughout the range of concentrations studied. The band at λ 4330 behaves exactly like the one at λ 4180, practically disappearing in A, Plate XII.

The band having its middle at λ 4445 is perhaps due entirely to the praseodymium present as an impurity. In A, Plate XI., it has about the same intensity as in a solution of praseodymium chloride having a concentration of 0.85 and a depth of absorbing layer of 3 mm. This indicates that the proportion of praseodymium in the neodymium salts used was about 6 per cent. The band at λ 4825, partly due to praseodymium, may also be seen throughout the entire series under consideration. Since the wave length of the praseodymium band is λ 4815, it is seen that neodymium has a band nearly coincident with that given by praseodymium, but lying a little closer to the red end of the spectrum.

The remaining praseodymium band has the position λ 4685, thus nearly coinciding with the rather narrow, strong neodymium band whose position is λ 4695.

The band which under A, Plate XI., was recorded as having the limits λ 4580 to λ 4650 shows in B as a hazy band with its center at λ 4615, together with a narrow, faint line at λ 4645. The band is visible in A, Plate XII., but has practically disappeared from view in B, of the same plate. The narrow line at λ 4645 does not show beyond B, Plate XI.

The band which in the table is recorded as λ 4740 to 4770 has in B, Plate XI., become a slightly hazy band having its middle at λ 4760. Its intensity is intermediate between that of the bands at λ 4695 and λ 4825, and hence like them may be seen faintly even in the plate corresponding to a dilute solution.

The band which in A, Plate XI., has the limits λ 5000 to λ 5330 breaks up on dilution into a rather complicated series of bands, some idea of which may perhaps be gained from the following: B, Plate XI., shows some absorption throughout the region given, but with a deep, narrow band at λ 5090 and faint transmission at λ 5100 and in the region λ 5150 to λ 5180. Absorption is complete from λ 5105 to λ 5150, and from λ 5180 to λ 5270. There is again incomplete absorption from λ 5270 to λ 5330, with indication of a band at λ 5315. In A, Plate XII., the general shading has the limits λ 5050 to λ 5330, and it shows the following: A narrow intense band at λ 5090; wide, hazy band at λ 5125; a pair of very intense, narrow bands at λ 5205 and λ 5222; very narrow band at λ 5255; and faint, hazy band at λ 5315. B, Plate XII., shows the shading diminished very much in intensity, and all the bands except the doublet λ 5205 to λ 5222 rather faint. The absorption in the doublet is still almost complete.

The limits of the yellow band in B, Plate XI., are λ 5700 to λ 5880 in the strip corresponding to the most concentrated solution. The band narrows by 30 Angström units on this spectrogram, the narrowing being due to a decrease in the shading towards the red, with decrease in concentration.

In B, Plate XII., the limits of the band are λ 5710 and λ 5840. There is still considerable shading, but it decreases only very slightly with dilution. The band begins to show its structure, but not well enough to allow any measurements to be made.

In B, Plate XII., the band has broken up into the following smaller bands: λ 5725, narrow and moderately intense; λ 5745 and λ 5765, double band, not clearly resolved, the red component being more intense than the violet. This double band is the most intense of the group. λ 5795, band having about the same intensity as the one at λ 5725, but being much wider and hazier; λ 5380, very faint band.

The group of absorption bands in the orange, given in the table, may be seen faintly in B, Plate XI., and very faintly in A, Plate XII., but, like the group in the red near λ 6800, it shows no further breaking up into more complicated bands on dilution.

B, Plate XI., shows that the spectrum ends at λ 7310 in what appears to be an absorption band. In Plate XII., it is seen that there is a very intense, narrow band at λ 7325; another narrow but fainter band at about λ 7350; and a wide, moderately intense band at λ 7390 or λ 7400, beyond which the plates were not sufficiently sensitive to give any appreciable photographic action with the length of exposure used.

The most intense bands of neodymium chloride, and hence the ones that would be most conspicuous in a very dilute solution, are the following: λ 3465, λ 3540, λ 4275, λ 5205, λ 5225, λ 5745, λ 5765, and λ 7325.

The wave lengths of all the bands, together with a brief description of the appearance of each band, are collected in the following table. It is to be understood that this table is not meant to represent what could be seen or photographed in any one solution of neodymium chloride in water. It merely records the position of all the bands which can be seen in a layer from 3 to 12 mm. deep, when the concentration is varied from 0 to 3.4 normal.

λ.	Character.
2900	About 20 A.U. wide
2985	About 25 A.U. wide
3225	Narrow and sharp
3390	Narrow, faint
3465	Very intense, narrow
3505	Rather wide
3540	Very intense, narrow
3560	Faint, narrow
4180	Faint, hazy
4275	Very intense and sharp
4290	Very narrow, faint
4330	Hazy edges
4615	Rather wide and hazy
4645	Very narrow, faint
4695	Narrow, intense
4760	Hazy edges, fairly narrow
4825	Narrow and fairly intense
5090	Narrow, intense
5125	Rather wide and hazy
5205	Very intense, narrow
5222	"
5255	Narrow, intense
5315	Hazy edges, faint
5725	Narrow, intense
5745	Very intense
5765	"
5795	Intense, moderately narrow
5830	Very faint and hazy
6235	Fairly narrow
6260	Very narrow, faint
6270–6310	Faint, hazy edges
6360–6390	"
6730	Faint band
6800	Moderately intense, hazy edges
6890	Hazy edges
7325	Very intense and narrow
7390	Rather wide band

Neodymium Chloride in Methyl Alcohol—Beer's Law (*See Plate XIII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.315, 0.25,

Plate XIII.
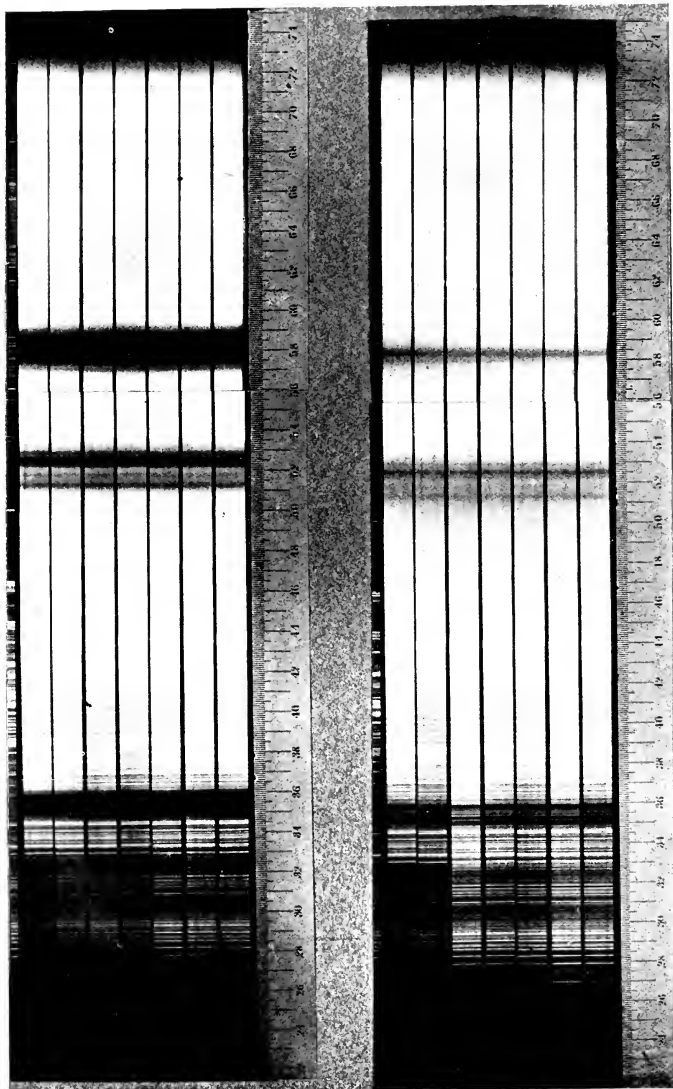
A

B

0.20, 0.16, and 0.125; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. The concentrations for B were, in the same order, 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as used in A.

There is some absorption in the extreme ultraviolet, which, however, is to be ascribed to the solvent and not to the neodymium chloride.

No trace of absorption due to the dissolved substance is visible until we reach the group of bands near λ 3500. There are three bands having their centers at λ 3475, λ 3505, and λ 3560. Of these the one at λ 3560 is the widest and also the most intense, while the one at λ 3475 is somewhat fainter than that at λ 3505. The bands are all much wider and hazier than those occurring near the same place in the aqueous solution. No change with dilution indicating a deviation from Beer's law can be detected in these or any of the other bands in the alcoholic solutions of the chloride.

In the violet and blue regions we find the following: A band at λ 4290, about 10 A.U. wide and only moderately intense. At λ 4325, a band somewhat wider and fainter. At λ 4460, a rather wide hazy band with a faint hazy companion towards the violet. This is the band which is perhaps due to praseodymium. The much greater concentration of the alcoholic solutions of praseodymium chloride studied in this work makes it impossible to verify this, by seeing whether the praseodymium band in dilute solution really has this general character.

There are bands at λ 4700, λ 4780, and λ 4825, all of about the same intensity, the one at λ 4770 being, however, much narrower than the other two, of which λ 4825 is somewhat the wider. Both λ 4700 and λ 4780 have faint companions towards the violet.

The group in the green is made up of six bands as follows: λ 5125, hazy and rather wide, moderately intense; 5180, also hazy but much fainter; λ 5220, moderately intense and narrow; λ 5245, intense, and with faint companion towards

the red; λ 5290, narrow and moderately intense, shading as far as λ 5330, with indications of a faint band at λ 5315.

The yellow group is made up of seven bands having the following characteristics: λ 5727, moderately intense with hazy edges; λ 5765, narrower, but not quite as intense as λ 5725; λ 5800, fairly narrow, strong; λ 5835, very intense; λ 5860, hazy and moderately intense, not clearly separated from λ 5835, shading to λ 5970, with two faint bands superimposed upon it, one at λ 5895 and the other at λ 5925.

No trace of bands is to be seen in the orange, but in the red there is a fairly narrow but faint band at λ 6860. The spectrum ends at λ 7355 in a deep, rather narrow band. It is evident that the spectrum of neodymium chloride when dissolved in methyl alcohol is quite different from its spectrum in aqueous solution, but this point will be taken up more fully in the discussion of Plates XV. and XVI.

Neodymium Chloride in Ethyl Alcohol—Beer's Law (See Plate XIV.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.315, 0.25, 0.20, 0.16, and 0.125; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B, the concentrations were 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as those used in A. The concentrations and depths of cell were, therefore, exactly the same as those in methyl alcohol, so that Plates XIII. and XIV. are directly comparable. A very careful comparison of the two plates reveals the remarkable fact that the two spectra are practically identical, the very slight differences noted being perhaps due to slight differences in development of the negatives.

In view of the great difference between either one of these spectra and that of the aqueous solution, this similarity is rather surprising, and it led us to think that perhaps in these alcoholic solutions we were getting the absorption of the neodymium chloride molecules themselves, while in the aqueous
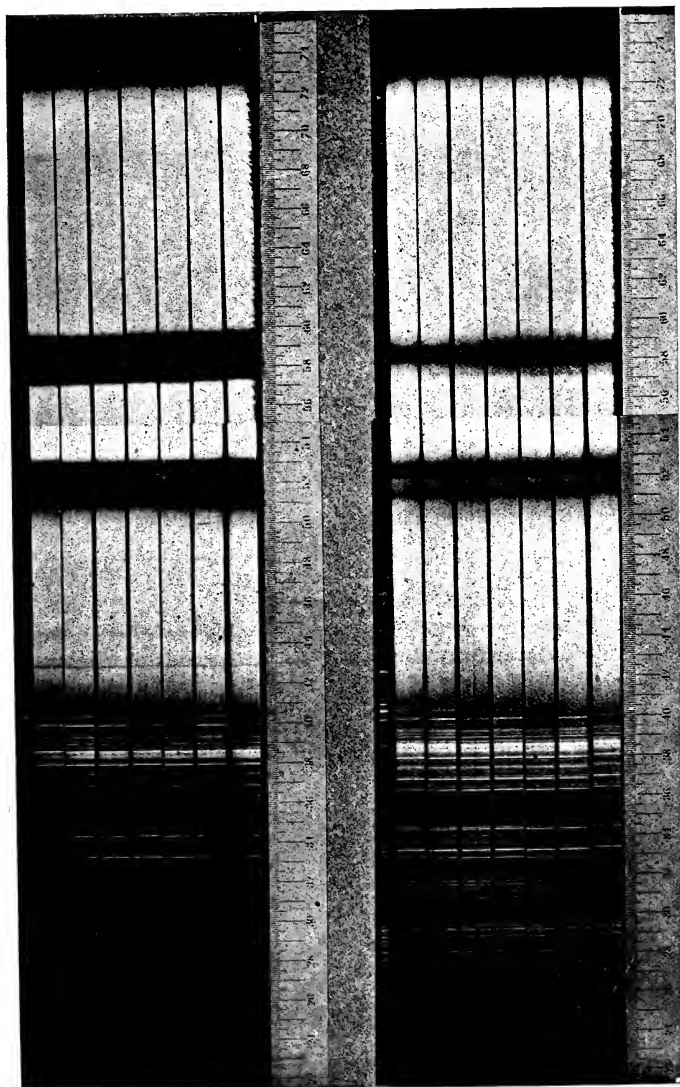
Plate XIV.

A

B

solution we get the absorption of some compound of the molecules with water. But that this is not the case was shown by the spectrum of anhydrous neodymium chloride (Plate XVII.), which is very different from that of any of the solutions. The spectrum of the alcoholic solutions is, therefore, not that of the NdCl$_3$ molecule *per se*, but must be that of some solvate of it or of the neodymium ion. But that solvates with methyl alcohol and ethyl alcohol should affect the frequencies of the vibrators in the metallic atom so very nearly in the same way seems a little surprising, to say the least, especially as solutions of the nitrate in the two solvents give somewhat different spectra, as will be fully discussed when we come to consider Plates XXI. and XXII.

The very slight differences between the bands shown in Plates XIII. and XIV. seemed to indicate that they were a little more hazy in the ethyl alcohol solutions, but the development of the negatives for Plate XIV. was not carried quite as far as was the case with those for Plate XIII., and this would tend to produce just the kind of difference that was noted.

Neodymium Chloride in Mixtures of Methyl Alcohol and Water
(See Plates XV. and XVI.).

Since, as we have just seen, the absorption spectrum of neodymium chloride in aqueous solution is so different from that of the alcoholic solutions, it was thought to be of some interest to see how the change from one to the other would take place if one of the solvents was made to displace the other gradually. A series of solutions was accordingly made up, the concentration of the dissolved salt being constant and equal to 0.5 normal, but the character of the solvent varied as follows: The percentages of water in the seven solutions were 0, 16.6, 33.3, 50, 66.6, 83.3, and 100; the corresponding percentages of methyl alcohol were 100, 83.3, 66.6, 50, 33.3, 16.6, and 0. Two spectrograms were made, namely, A, Plate XV., where the depth of the cell was 1.5 cm., and B, where the cell had a depth of only 5 mm. A was made in order to show clearly the change taking place in the narrower

and fainter bands, while B was intended to show the change
of structure of the more intense bands, such as the green
and yellow ones. The strip which is adjacent to the num-
bered scale belongs to the solution in pure water, while the
one nearest the narrow, comparison spark spectrum belongs
to the solution in pure methyl alcohol.

Plate XV. shows that, beginning with the strip nearest
the scale, the first six spectra are very nearly identical. From
the sixth to the seventh there is an abrupt change, which
at first sight consists in a shift of all the bands towards the
red, but which on closer examination is seen really to con-
sist in a disappearance of one spectrum and the appearance
of the other. Since the first strip is the spectrum of the solu-
tion in pure water, and the sixth is nearly identical with the
first, it follows that as large a proportion of alcohol as 83
per cent in the solvent does not change the absorption spec-
trum materially; the chief change takes place when the per-
centage of alcohol is varied from 83 per cent to 100 per cent.

It is to be noted that the apparent shift of the bands towards
the red is in reality not quite as great as it appears to be at
first sight from Plate XV., owing to the fact that the film ac-
cidentally shifted slightly towards the red between the sixth
and seventh exposures. The amount of this mechanical
shift is easily seen, however, by comparing the spark lines
in the ultraviolet. A measurement of the shift shows that
it is approximately 3 Angström units, and the same for both
A and B, while the "apparent" shift of the absorption line
at λ 4275 in aqueous solution is actually 15 Angström units,
its position in the alcoholic solution being 4290.

The slight changes taking place in some of the bands
throughout the spectrograms of Plate XV. are perhaps suffi-
ciently clear in the reproductions. However, as a good deal
of the detail shown by the negatives is lost even in the most
perfect processes of reproduction, we give here a description
of the changes taking place in two of the bands as seen on
the original negative. We select the bands at λ 4275 and
λ 4760 from the negative for A, Plate XV.

In the aqueous solution the λ 4275 band is very intense

Plate XV.

A

B
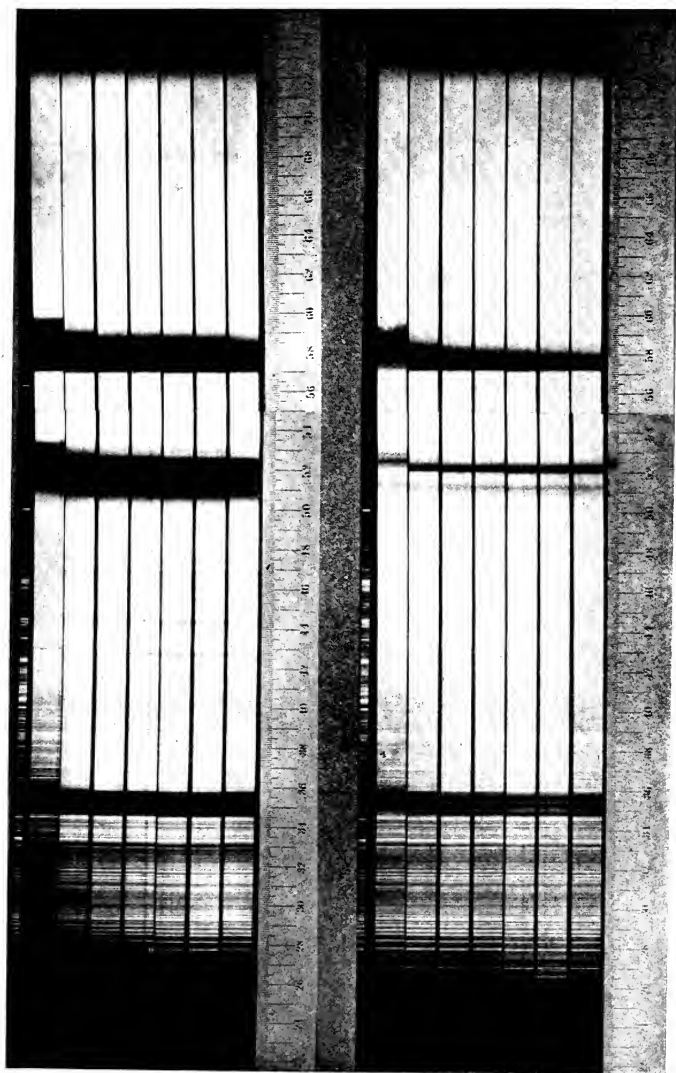
and narrow, its whole width being less than 5 Angström units. The edges are only very slightly shaded. In the alcoholic solution the position of the center of the corresponding band is λ 4290. It has a width of from 12 to 13 Angström units, and is not nearly as intense as in the aqueous solution.

Throughout the first six strips the λ 4275 band maintains its position and intensity almost unchanged. Its position does not change in the least, but its intensity in the sixth strip is a trifle less than in the others. In the seventh strip there is not the faintest trace of it left. In the third strip, corresponding to the solution whose alcohol content was 33.3 per cent, there appears at λ 4285 an extremely faint and narrow line. In the fourth strip it is somewhat wider and more intense, but its center is still at λ 4285. In the fifth strip it is beginning to be fairly conspicuous, and in the sixth it is a band of moderate intensity, having its center at about λ 4287. This band is undoubtedly the same one which in the pure alcoholic solution has its center at λ 4290 or very near there, the exact wave length being perhaps nearer to λ 4292. We see, then, that even when the mixed solvent contains only about one-half alcohol, this band exists independently of and distinct from the band characteristic of the aqueous solution; that it is at first only a very narrow and faint line, which widens towards the red as the percentage of alcohol is increased.

The band whose center is at λ 4760 has the following appearance in the aqueous solution: Faint absorption begins at λ 4748 and rises rapidly to a maximum between λ 4755 and λ 4760, then decreases slowly to nothing at λ 4775. The band is accordingly a trifle asymmetrical, the slope towards the violet being considerably steeper than that towards the red. The corresponding band in the alcoholic solution is double and answers the following description: Very faint absorption begins at λ 4753, and rises to a faint maximum at about λ 4757, becoming again zero at λ 4760. It begins again at λ 4772, rises rapidly to a strong maximum at λ 4780, and falls to zero at λ 4790. The component whose center is at λ 4757 is very faint compared with the main band.

In the first and second strips we have nothing but the band corresponding to the aqueous solution. In the third strip the red side of the band has increased slightly in intensity, making it appear much more nearly symmetrical. This change increases in the fourth and fifth strips, the band at the same time widening considerably. In the sixth strip its appearance is as follows: Absorption begins at λ 4748 and rises to a maximum just to the violet side of λ 4760, then decreases slightly towards λ 4770, after which it increases somewhat to λ 4778, then falls off to zero at λ 4787. It is very evident from a study of the change in this band that the two bands characteristic of the aqueous and alcoholic solutions coexist, and that the band appearing in our photographic strip is the sum of the two taken in different proportions, the proportion of the alcohol band being, however, very much smaller than the proportion of alcohol in the corresponding solution. A similar description might be given for any one of the other bands, but this is not necessary, as the changes are of exactly the same nature as those we have already indicated. In every case where the alcoholic solution has a strong band which differs somewhat in position from any band in the aqueous solution, we begin to see traces of this band when the proportion of alcohol in the mixture reaches 50 per cent; but the band remains comparatively faint even when the proportion is as high as 83.3 per cent.

In order to study more carefully the change which takes place between the sixth and seventh strips of the spectrograms of Plate XV., a series of alcoholic solutions was prepared containing the following percentages of water: 0, 2.6, 5.3, 8, 10.6, 13.3 and 16. The concentration of the neodymium chloride was constant and equal to 0.5 normal. Two spectrograms were made, one with a depth of absorbing layer of 1.5 cm. in order to show the fainter bands, and the other with the depth of the cell of only 5 mm. in order to show as much as possible of the structure of the larger bands. The first spectrogram is reproduced in Plate XVI., A, and the second in Plate XVI., B. The strips corresponding to the pure alcohol solutions are adjacent to the numbered scale, the spec-
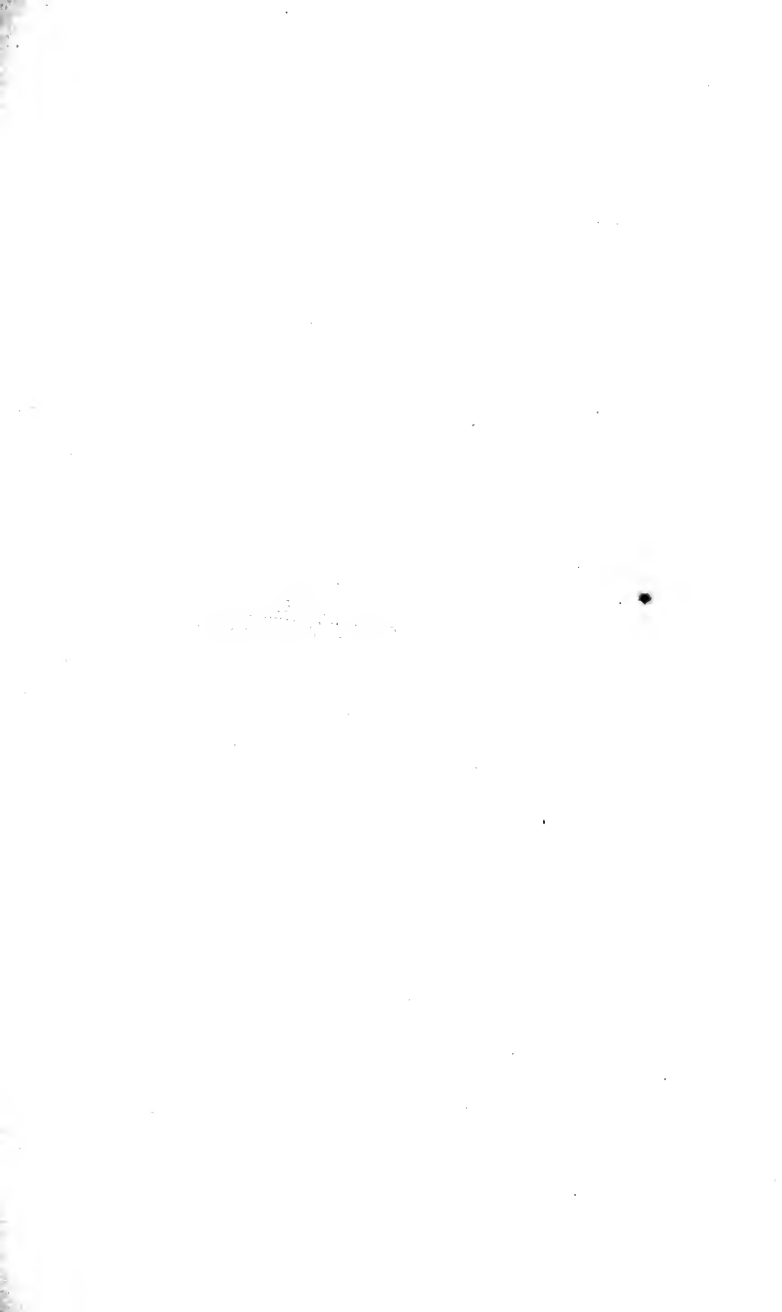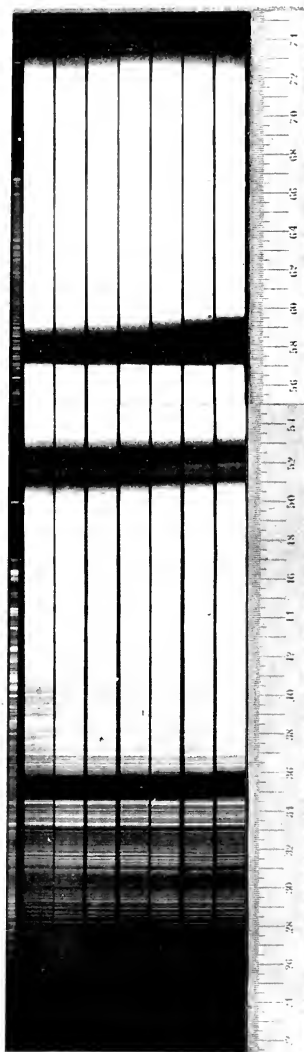
Plate XVI.

A
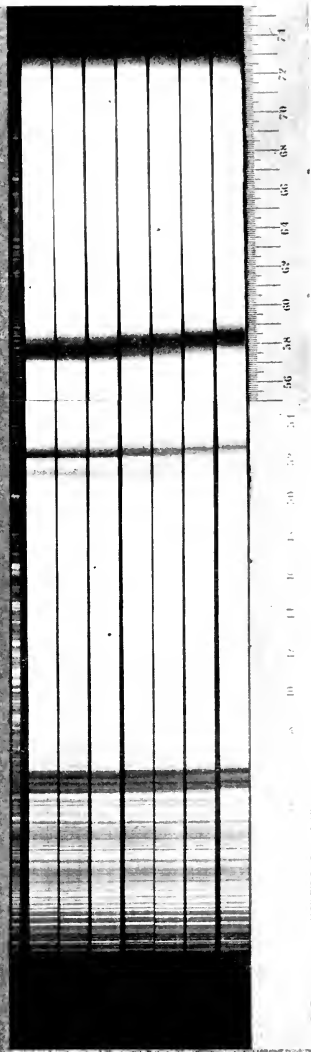
B

trum of the solution containing 16 per cent water being next to the comparison spark spectrum.

Although we found, in considering Plate XV., that some slight change in the spectrum takes place when the percentage of alcohol is changed from 0 to 83 per cent, yet this change is so small, and the bands due to the aqueous solution are so strong, that we may regard the spectrum of a solution containing 16 per cent of water as practically that of the aqueous solution. Accordingly, the spectrograms on Plate XVI. may be taken to show very nearly the whole change which takes place when the solvent of neodymium chloride is gradually changed from pure water to pure methyl alcohol.

In A the ultra violet is rather too intense to allow its structure to be seen. Accordingly, we see the whole band remain sensibly unchanged as the water is varied from 16 per cent to 8 per cent, and it shifts towards the red with increasing rapidity as the water is reduced to zero, the whole apparent shift amounting to about 20 Angström units. On the negative the intense band at λ 3465 may be clearly seen, however, and its intensity decreases very slowly from the first to the third strips, counting from the narrow, comparison spark spectrum. In the fourth strip its intensity is about half of what it was in the first strip, and from this it decreases rapidly, vanishing entirely in the strip nearest the scale.

In B the structure of this band is seen very distinctly, and we find that the bands characteristic of the aqueous solution gradually decrease in intensity, especially from the third to the fourth strips, while the wider bands, characteristic of the alcoholic solutions, increase in intensity, the two sets existing together. The change in the band at λ 4275 is the one that shows the best, because here the two bands belonging to the aqueous and alcoholic solutions, respectively, are both intense and narrow and clearly separated from one another.

The alcoholic band is clearly visible in the first strip, and it increases continuously in intensity as the amount of water is decreased, but more rapidly from the fourth to the seventh strips than from the first to the fourth. Its position also

shifts somewhat towards the red from the first to the fourth strips, the wave lengths of its center for the two strips being λ 4287 and λ 4292, respectively. Accompanying this shift is a change in its character, which may be made clear by the following statements: In the first strip it has the appearance of an unsymmetrical band, the maximum intensity being nearer the violet. In the third strip it extends from λ 4280 to λ 4295, and has about the same intensity throughout. In the fourth strip the intensity of its violet edge has decreased while that of the red edge has increased considerably, giving the band an unsymmetrical appearance, with the maximum intensity towards the red. In the fifth strip the violet shading from λ 4280 to about λ 4284 has disappeared, leaving a band very nearly symmetrical about λ 4290. It appears, therefore, that we are really dealing with two unresolved bands, one having its center at about λ 4285 and the other at λ 4292.

The band at λ 4275, due to the aqueous solution, decreases in intensity throughout, but more rapidly from the third to the sixth strips than at first. Its position remains the same throughout. As near as the eye can judge the intensity of this band is reduced to about half-value when the fourth strip, corresponding to 8 per cent of water in the solution, is reached. The alcohol band at λ 4292 also has about 50 per cent of its final intensity in the same solution.

The band at λ 4760 shows the same kind of a change that we described in some detail above, only here the change is much more gradual and easy to follow. It also shows about equal intensity for the two sets of bands when the amount of water is 8 per cent of the whole

The green and yellow bands are not sufficiently resolved in A to allow the change in the individual bands to be followed, and hence these apparently show only a gradual shift towards the red with decrease in the amount of water. In B, however, they are both sufficiently resolved to enable us to follow the change in each individual band, although this is a little difficult in some cases on account of the large number and the incompleteness of separation of the bands. The

change is in every respect the same as we have found for the other bands, namely, the bands due to the aqueous solution diminish in intensity, and reach about half-value in the 8 per cent water solution, while those belonging to the alcoholic solution increase in intensity as the amount of water is decreased.

The band in the red near λ 6800 shows the change very well indeed, the "water" band having the position λ 6800, while that pertaining to the alcoholic solution is situated at λ 6860, and hence the two are well separated. Here the point of equal intensity appears to be reached in the solution containing 10.6 per cent of water, but this is due to the fact that the alcoholic band has a considerably greater intensity than that of the aqueous solution, the conditions as to concentration and depth of layer being the same. Taking this into account, it is seen that this band obeys substantially the same rule as the others.

The change in the band at λ 7325 is more difficult to follow on account of the small intensity of the photographic action on the less refrangible side of this position. The band belonging to the aqueous solution may be seen very clearly even in the strip corresponding to the 2.6 per cent water solution, but is, of course, entirely absent in the alcoholic solution. Its intensity in the 2 per cent solution, however, seems a little greater than we should expect from the behavior of the other bands, but this is perhaps due to the rather weak photographic action in this part of the spectrum, combined with the great intrinsic intensity of the band. The alcoholic solution transmits light as far as λ 7355, where its spectrum ends abruptly in a band.

Throughout this description we have laid great stress on the fact that on Plate XVI. the two sets of bands coexist, the bands due to the aqueous solution decreasing, while those belonging to the alcoholic solution increase in intensity with decrease in the percentage of water; we have also called attention to the fact that the two sets of bands have about half their full intensity in a solution containing about 8 per cent of water. This was for a 0.5 normal solution.

The next question which suggested itself was whether the composition of the solvent which gives the two sets of bands with about half their normal intensity is independent of the concentration of the dissolved substance. If this were the case, then we should have to conclude that the determining factor is the nature of the solvent; while if the requisite composition of the solvent depends upon the concentration the ratio between the amount of dissolved substance and one or other of the solvents would perhaps be the important thing. To answer this question a set of solutions was made up in which the solvent was kept exactly the same as it was for the solutions used in making the negatives for Plate XVI., but the concentration of neodymium chloride was made 0.25 normal instead of 0.5 normal. In order to have this spectrogram directly comparable with B, Plate XVI., the depth of cell was kept at 1.0 cm. throughout.

A study of the negative showed that the two sets of bands have about half their normal intensity in the third strip, counting from the numbered scale, corresponding to 5.3 per cent of water. In the fourth strip the bands characteristic of the alcoholic solutions are very weak compared with the bands belonging to the aqueous solution, while in the second strip the opposite is the case. It is plain, therefore, that the composition of the solvent which gives the two sets of bands with about half their normal intensity depends upon the concentration, and it also seems very probable that, provided the ratio of water to dissolved substance is kept constant, the two sets of bands will not vary much in relative intensity. A simple calculation shows that in the solutions which produced the bands with about half their normal intensity, there were present approximately 10 molecules of water to 1 molecule of neodymium chloride.

Neodymium Chloride—Anhydrous (See Plate XVII.).

This plate was made in order to see whether the spectrum of the anhydrous salt is identical with that observed when the salt is dissolved in pure methyl or ethyl alcohol. The anhydrous salt was in the form of a very fine powder and was con-

tained in a bottle with a tight-fitting glass stopper. An image of the Nernst filament was thrown on the surface of the powder in contact with the walls of the bottle, and this image was in turn focussed on the slit of the spectroscope by means of the concave spectrum mirror. The light falling on the grating was necessarily very faint, therefore rather long exposures were necessary; but this caused no inconvenience, since the Nernst lamp burns so steadily that it needed no attention whatever. In order to show as well as possible both the strong and the weak bands, a series of exposures was made on the same film, the times of exposure, beginning with the strip nearest the numbered scale, being 30 minutes, 1 hour, 1.5 hours, 2 hours, and 2.5 hours. On account of the fact that the beam of light had to pass through the glass condensing lenses, as well as the glass walls of the containing bottle, the spectrum ends at about λ 3450 for the strip nearest the comparison spectrum, and at λ 3600 for the one nearest the scale.

The comparison spark spectrum in this case was made by using zinc terminals instead of the carbon terminals employed throughout the rest of the work. Since there is usually some accidental shift between the successive strips on a film, and since no light but that of the Nernst filament was used in making the five strips on Plate XVII., it is evident that no accurate wave length measurements could be made by a comparison with the spark spectrum on this plate. In fact, the position of a given absorption line, which appeared both on the film and on the red-sensitive plate, was found to differ by as much as 10 Angström units as measured from the two negatives. Hence it was necessary to determine the position of one or more of the absorption lines by comparison with a spark spectrum which had been impressed on the plate without moving this between the exposures to the light reflected from the chloride powder and to that from the zinc spark. This was accomplished by making an exposure of about an hour for the absorption spectrum and then, without moving the plate holder, impressing the ultraviolet portion of the spark spectrum on the same strip. Thus, the positions of a

few of the strongest and sharpest absorption bands are determined, and the positions of the others were measured by determining their distances from the standards.

On the whole, the spectrum is similar to that observed in solutions; that is, if the solutions show a group of absorption bands in a certain region, then there is also a group of bands in nearly the same place in the spectrum of the light reflected from the anhydrous salt; but as a rule, the individual bands in the group are much narrower and more numerous in the latter than in the former. This agrees with what has previously been found by Becquerel[1] and by one of us.[2]

In the following table, the position and character of the stronger bands are given. No attention was paid to the numerous bands which are so faint as to require special precautions in order to set on them, as the object of the present work was not so much to catalogue the spectra as to try to get some idea as to the causes of the changes which take place when the substance is subjected to different conditions.

λ.	Character.
3500	Rather strong, narrow band
3537	Weaker and wider
3570	Narrow and intense
3595	Narrow and very intense
3612	Rather faint and hazy
4045	Weak and hazy. Perhaps 2 or 3 bands
4080	More intense, but hazy
4210	Faint, narrow
4228	Faint, perhaps 2 bands
4308	Very narrow and intense
4313	"
4333	Wider and a little hazy, but intense
4357	Narrow, shaded towards red
4455	Wide and hazy
4500	"
4640	Faint, hazy
4680	Faint, hazy
4717	Narrow and moderately intense
4725	"
4735	"

[1] H. Becquerel: Ann. Chim. Phys. [6], **14**, pp. 257 *et seq.*
[2] J. A. Anderson: Astro-Phys., J., **26**, pp. 73-94 (1907).

Plate XVII.

λ.	Character.
4775–4790	Sharp on violet side, perhaps 2 bands
4815	Rather narrow
4855	Intense and narrow
4872	Weak
4888	Narrow, and moderately intense
4895	"
5000–5370	Strong general absorption
5088	Weak, slightly hazy
5117	Stronger, shaded somewhat
5147	Narrow, intense, hazy on violet edge
5174	Intense, slightly hazy
5183	Not as narrow as 5174
5216	Shaded to violet
5254	Very intense and narrow
5267	"
5282	Weaker and wider than the last two
5300	Shaded towards red, perhaps double
5328	Intense, narrow
5342	Weaker and broader
5760–6000	Strong general absorption
5768–5782	Very intense, double band
5807	Narrow and intense
5829	Most intense band in spectrum
5858	Very narrow
5875	A little hazy
5890	Weak
5902	Fairly narrow and intense
5922	Hazy and faint
5946	Narrow, intense
5968	Wide, faint, and hazy
6265	Wide, moderately intense
6290	Narrow, faint
6325	"
6375	"
6775	Wide, faint
6796	Narrow, faint
6815	"
6838	Moderately intense
6860–6900	Band, shading towards red
6922	Moderately intense
7422	Narrow, intense band

It is, of course, evident that the spectrum of the solutions of neodymium chloride dissolved in methyl or ethyl alcohol

is very different from that of the andydrous salt. It seems reasonable to suppose that if the molecules of the salt in the nonaqueous solutions exist in the free state, that is, not combined with the solvent in any way, they should give about the same spectrum as they do when in the state of the dry powder. Since they do not do this, we must suppose that the solvent plays an important rôle in determining the character of the absorption, and how it can do this without being combined with the salt in some way is not easy to understand.

Neodymium Bromide in Water—Beer's Law (See Plate XVIII.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.3, 1.7, 1.15, 0.77, 0.54, 0.38, and 0.29; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.57, 0.42, 0.29, 0.19, 0.13 0.09, and 0.07; the depths of the absorbing layer were the same as in A.

The bromide solutions are very much redder in color than those of the chloride or nitrate. Judging from the color alone, one would say that the nitrate solutions are much more transparent in the blue and violet than the chloride, and the chloride solutions much more so than those of the bromide. The spectrograms do not show this, at least not very clearly, which merely indicates that where full exposures are given, slight general absorption is not recorded by the photographic plate. A spectrophotometric comparison of the light transmitted through these solutions, such as is now in progress in the present work, will undoubtedly show this general absorption of the bromide solutions in the more refrangible portion of the spectrum.

In studying the spectrograms of this plate, A was compared with Plate XI., B, and B with Plate XII., B; that is, the spectrum of the bromide solutions was compared with that of a chloride solution whose concentration, in each case, was almost exactly 1.5 times that of the bromide solution, the depth of the absorbing layer being the same in both cases. The two spectra are found to be almost identical, except in

Plate XVIII.
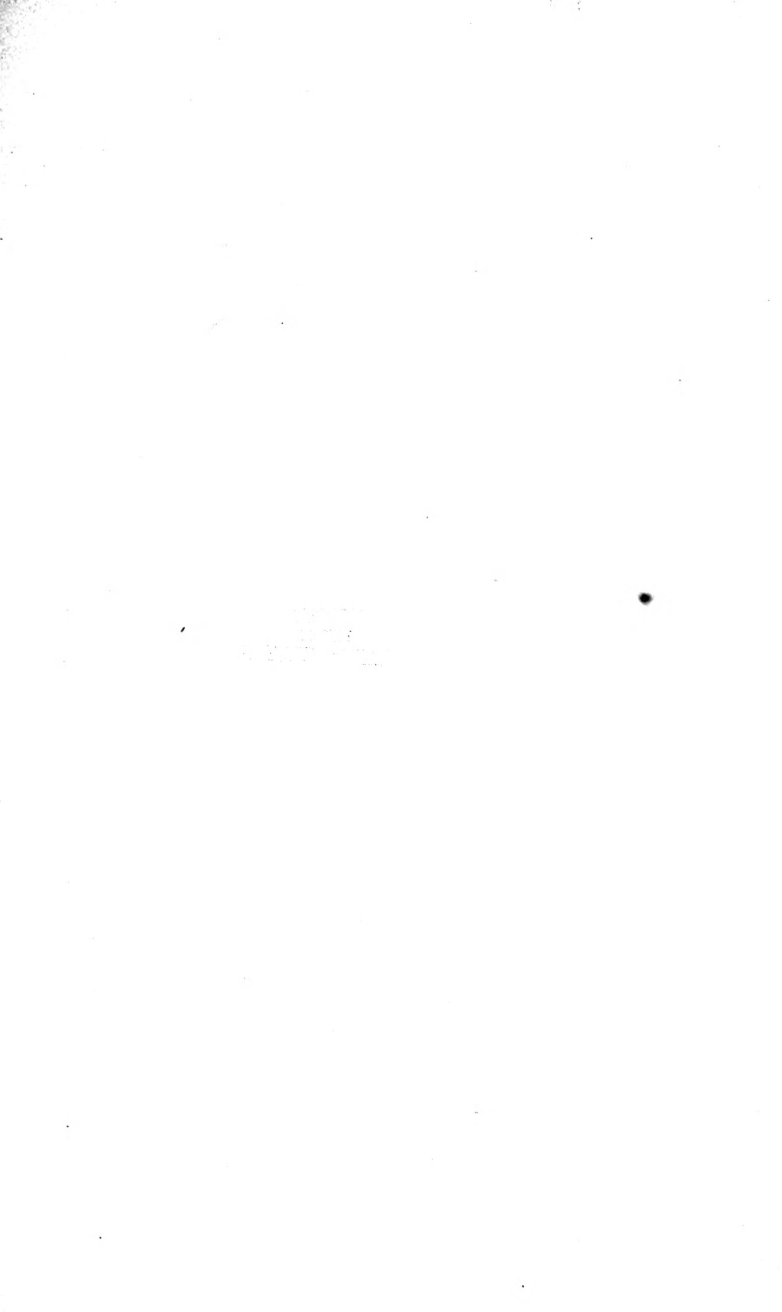
the extreme ultraviolet, where the bromide solutions absorb much more strongly. The limits of transmission for the most concentrated and most dilute solutions of A are λ 3270 and λ 3050, respectively, whereas the corresponding chloride solutions transmitted to beyond λ 2500. The ultraviolet absorption shown by B is about the same as that of the chloride solutions used in making Plate XI., B.

The absorption bands have in general about the same intensity and character in the bromide solutions as they have in the corresponding solutions of the chloride, indicating a considerably greater absorbing power of the bromide, since the concentrations of its solutions were only 0.66 of that of the chloride. A small part of this is due to the fact that the negatives of Plate XV. were not as fully developed as those made with the chloride solutions, but even if the development had been exactly the same, the bands of the bromide solutions would only have been very slightly less intense than those of the chloride solutions, so we must conclude that in solutions of the same concentration the bands of the chloride solution would have only about 75 per cent of the intensity of the same bands in the spectrum of the solution of the bromide.

It will be remembered that the very concentrated solutions of the chloride showed some slight deviations from Beer's law, the absorption to the red side of the narrow band at λ 4275 being described in some detail. The deviations from Beer's law are smaller in the bromide solutions, perhaps because the concentrations are less. No shading or fine absorption line between λ 4275 and λ 4290 is to be seen in the spectra of even the most concentrated solutions used in making the negative for A of Plate XVIII. The shading on the red side of the yellow band narrows somewhat with increasing dilution, but not quite as rapidly as was the case with the chloride.

Neodymium bromide was dehydrated in a current of hydrobromic acid and dissolved in methyl alcohol, and also in mixtures of methyl alcohol and water. The solution in methyl alcohol was stable, and showed the same spectrum as a solution of the chloride in the same solvent. On adding water,

precipitates were formed, indicating some chemical change. These were filtered out and a spectrogram made to see whether the same changes that we observed with the chloride take place in this case. This spectrogram is not reproduced, but it indicated that the changes which were produced were, quantitatively as well as qualitatively, the same as those we discussed under Plates XV. and XVI.

Neodymium Nitrate in Water—Beer's Law (See Plates XIX. and XX.).

The concentrations of the solutions used in making the negative for A, Plate XIX., beginning with the one whose spectrum is adjacent to the numbered scale, were 2.96, 2.22, 1.48, 0.99, 0.69, 0.50, and 0.38. For B the concentrations were 1.48, 1.11, 0.74, 0.50, 0.35, 0.25, and 0.19. For A, Plate XX., they were 0.74, 0.55, 0.37, 0.25, 0.175, 0.125, and 0.095; and for B, 0.37, 0.275, 0.185, 0.125, 0.092, 0.062, and 0.048. The depths of absorbing layer were in each case 3, 4, 6, 9, 13, 18, and 24 mm.

The nitrate solutions are much less yellow than the chloride solutions, having, when concentrated, a decided pinkish tint, indicating greater transparency in the violet region of the spectrum.

The spectrum of the nitrate solutions, especially when the concentration is considerable, differs quite a little from that of the chloride. It is true that at first glance they seem identical, for wherever there is a band in the spectrum of the chloride solution a band is found in the nitrate solution; but, at least in concentrated solutions, the bands have a very different appearance. The general difference is that the nitrate bands are much broader and hazier than those observed with the chloride. With dilution the spectrum of the nitrate changes very much more than that of the chloride, which we found was practically unchanged when the concentrations were varied from about 1.5 normal to near zero. The spectrum of the nitrate solutions changes somewhat, even in B, Plate XX., where the concentration ranges from 0.37 to 0.048 normal.

Plate XIX.
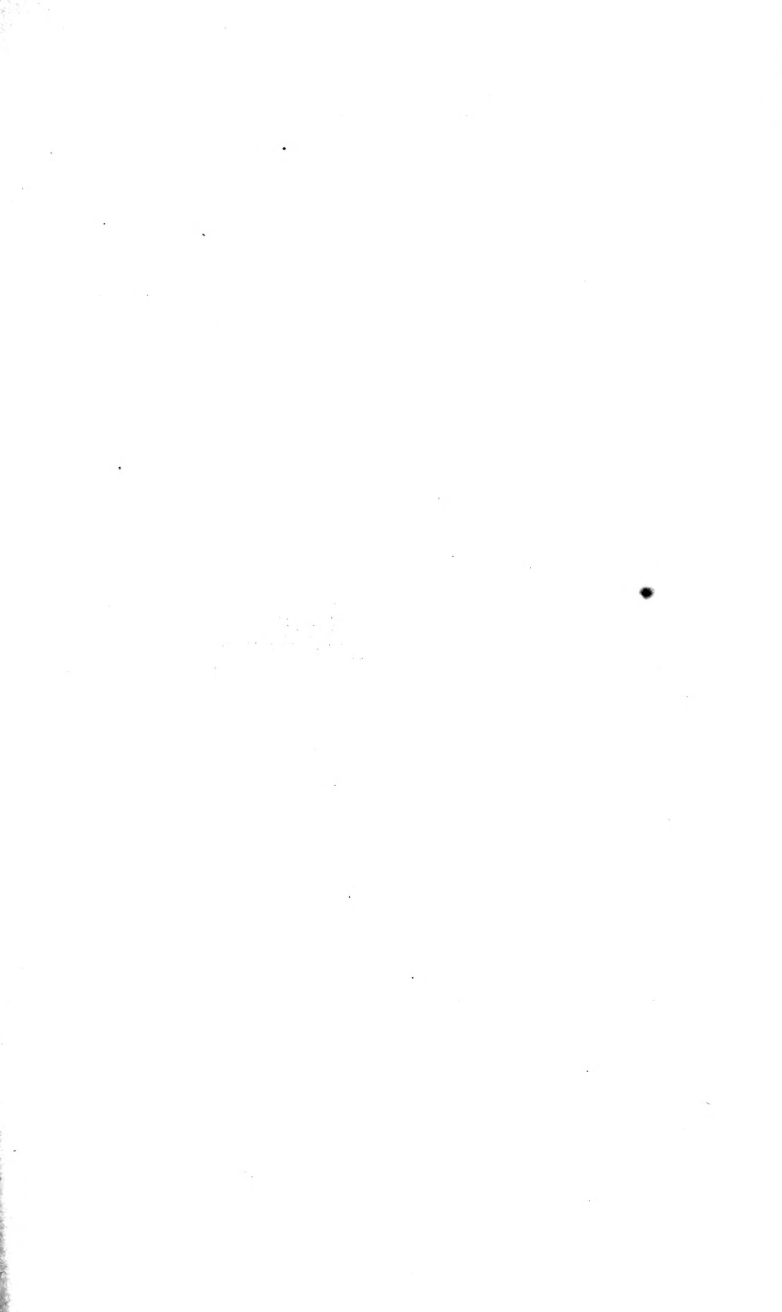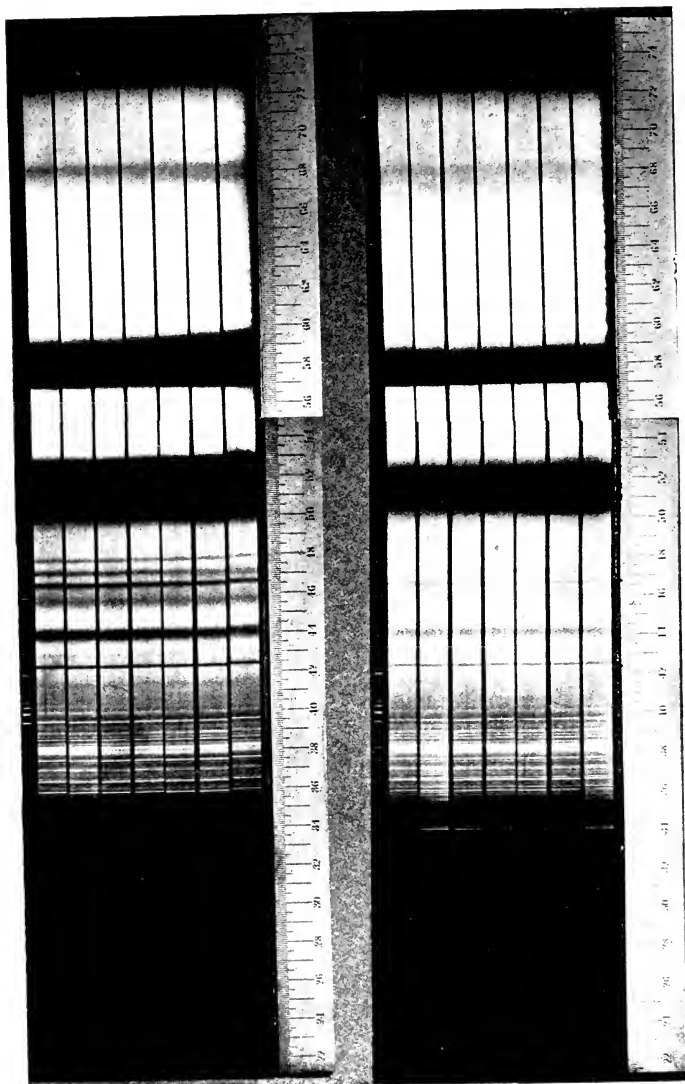
A

B

Instead of giving a detailed description of the spectrum of the nitrate, we will limit ourselves to a description of the changes which take place in a few of the bands differing most from the corresponding bands in the spectrum of the chloride solution.

Let us consider first the band at λ 4275. In the spectrum of the chloride solution this band has a width of only a few Ångström units, and is very intense. In the most concentrated nitrate solution this band has a width of 15 A.U. and its center falls at about λ 4280. Its edges are rather hazy, but the band is very nearly symmetrical. With increasing dilution the violet edge increases in intensity, taking more and more the form of a narrow absorption line with center at λ 4275, while the red portion of the band decreases in intensity, and at a concentration of 0.38 and a depth of layer of 24 mm. it has taken the form of a slightly hazy band with its center near λ 4282. This band is here clearly separated from the more intense and narrow one at λ 4275. With a concentration of 0.19 normal and a layer 24 mm. deep, the λ 4282 band has become a mere shade on the red side of the λ 4275 band, and finally, with a concentration of 0.048 and a 24 mm. layer of the solution, it is no longer visible on the photograph.

At λ 4330 or λ 4335 the concentrated chloride solutions show a rather wide hazy band, the intensity of which is not sufficient to allow it to be seen in solutions of less than 1.0 normal with a depth of layer of 5 mm. or less. The more dilute solutions of the nitrate used in making A, Plate XIX., show this band with about the same intensity and character that it has in solutions of the chloride, while the very concentrated nitrate solutions show it very faintly; that is, the band increases in intensity with dilution. In fact, it behaves very much like the λ 4275 band, indicating that the two owe their origin to the same "absorber."

The 3.4 normal chloride solution in a layer 3 mm. deep shows a band at λ 4760, to which the following description applies: Absorption begins at λ 4750, rises gradually to a maximum at λ 4760, then gradually falls to zero at λ 4770. This band remains practically constant throughout the series

of solutions used in making B, Plate XI., showing that it is practically unaffected by change in concentration.

The 2.96 normal solution of the nitrate, with a layer 3 mm. deep, shows, in the same region, a band which has the following characteristics: Absorption begins at λ 4730, rises to a maximum at λ 4737, then falls to a slight minimum at λ 4742, from which it again rises to a maximum at λ 4755, falling off gradually to zero at λ 4780, with indications of a faint minimum near λ 4765. We really have then to deal with a group of three bands, their centers being approximately at λ 4737, λ 4755, and λ 4772. With dilution the bands at λ 4737 and λ 4772 rapidly lose their identity, while the band whose center was at λ 4755 increases in intensity and somewhat asymmetrically; so that in the solution whose concentration was 0.99, with a depth of layer of 9 mm., there remained but a single band, having its center at λ 4760, and shading off towards both sides a little more than the corresponding band in the chloride solution. With increasing dilution this band also becomes more and more like the λ 4760 chloride band.

The chloride solution whose concentration was 1.7 normal, with a layer 3 mm. deep, showed a deep, narrow absorption band at λ 5090, and a wide, somewhat hazy one with its center at λ 5125. There was a region of transmission between the two about 15 A.U. wide. A, Plate XVI., shows that these bands do not change materially with dilution to 0.22 normal. The corresponding nitrate solution also shows a band at λ 5090, but it is much wider and hazier than in the chloride solution, while the λ 5125 band is, if anything, narrower. The two bands are not clearly separated in the first strip of B, Plate XIX. With dilution, however, the λ 5090 band narrows down and becomes a little fainter, while the λ 5125 band widens a little towards the red, so that in rather dilute solutions the bands present the same appearance as they do in the corresponding chloride solutions. The region λ 5200 to λ 5240 shows practically continuous absorption with very hazy edges in the first strip of B, Plate XIX.; with dilution this changes rapidly, indicating bands somewhat similar to those of the chloride solutions belonging to A, Plate XII.
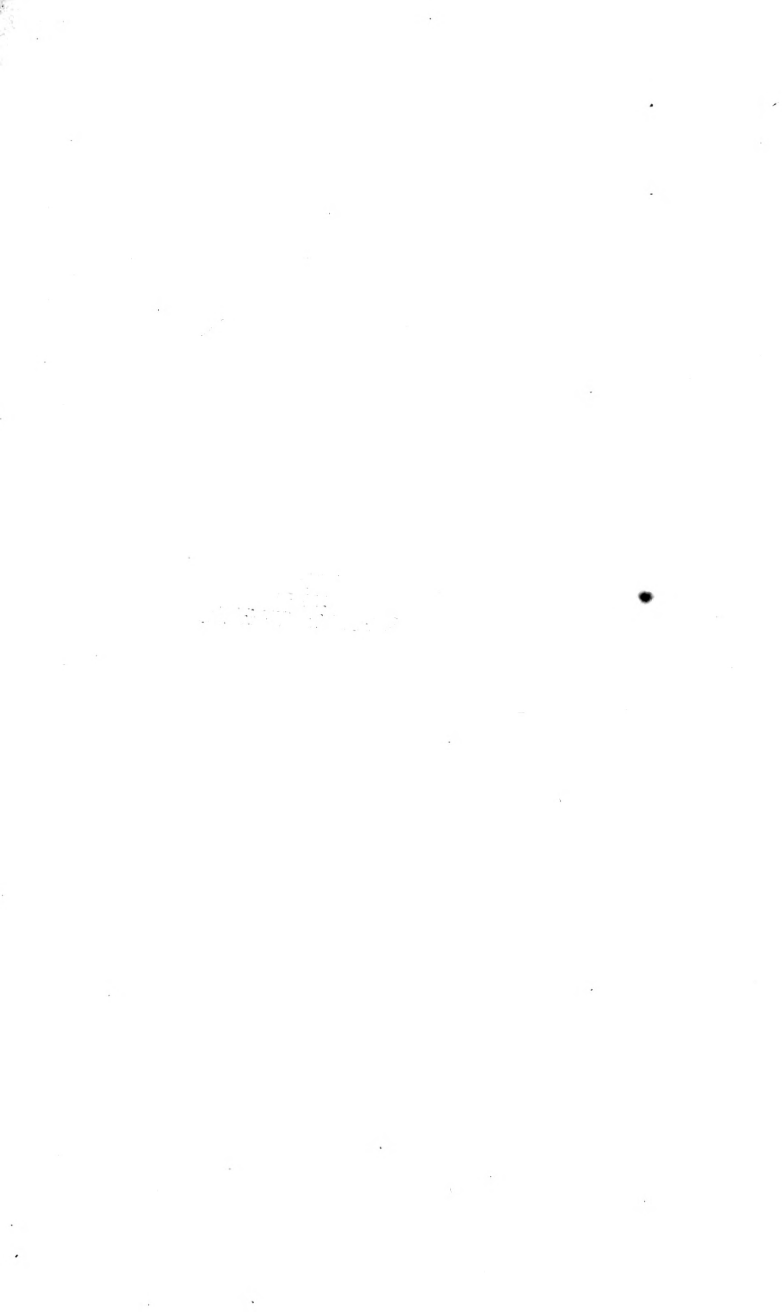
Plate XX

In A, Plate XX., the band has broken up, and instead of showing two narrow intense bands at λ 5205 and λ 5222 it shows the following: There is a deep, narrow band at λ 5205, a wider and very much more intense one at λ 5225, and a rather narrow, intense band at λ 5235. With increasing dilution the λ 5235 band diminishes in intensity, practically disappearing in the most dilute solution used in making B, Plate XX. At the same time λ 5225 decreases somewhat in intensity and rather more on the red than on the violet side, so that when the most dilute solution of B, Plate XX., is reached its intensity is only slightly greater than that of the λ 5205 band and its center is at about λ 5222. Here also, then, we find the same general tendency for the spectrum of the nitrate solutions to change with dilution so as to become more and more like that of the chloride and bromide solutions.

We might go on and give in detail the changes taking place in the bands located in the yellow, orange, and red, since the changes here are just as well marked as those we have already described. But they all point to the same thing, namely, the dissimilarity of the spectra of concentrated solutions, and the gradual change of the nitrate spectrum into that of the chloride or bromide with decreasing concentration. That the spectra of dilute solutions should become more and more alike with increasing dilution was, of course, to be expected from the theory of dissociation; but on the simple theory of dissociation no one could have predicted that the chloride and bromide should give spectra which are practically identical, both in concentrated and in dilute solutions, while the nitrate should behave so differently, especially as it is well known that the three dry salts have quite different absorption spectra.

Our work on the spectrum of neodymium chloride in mixtures of alcohol and water made it seem very probable that the molecules as well as ions of the salt in solution are solvated, that is, have combined with them a relatively large number of molecules of the solvent. On this view, the results with aqueous solutions of the chloride, bromide, and nitrate are just about what we ought to expect, if we assume that the absorption bands are due to electrons which are located

in, or closely associated with the neodymium atom. Let us consider this a little more fully, even at the risk of repeating certain things we have said before.

Let the neodymium atom contain electrons which, if the atom is by itself, would respond to light waves of certain definite frequencies. White light, after having been acted on by a number of such atoms, would, when analyzed by a prism or grating, show a certain number of absorption bands whose wave lengths could be determined. If, now, the atoms, instead of being free, are each united to 3 chlorine atoms, these foreign atoms would affect the periods of the neodymium electrons and we should expect to find the absorption spectrum modified. If the neodymium atom were combined with 3 bromine atoms instead of chlorine, we should expect a somewhat different spectrum again, and so on for the various salts; each one would be characterized by its own absorption spectrum. If these salts could be dissolved in some medium which had no action on them other than to allow their molecules to move about freely, we should not expect any material change in the spectrum, while if the solvent united with them, forming solvates, we should expect the spectrum to be modified.

In a solvent like water, where it is probable that rather complex hydrates are formed, the effect of the solvent might even become *the* most important factor in determining the character of the absorption. To take a concrete case, suppose each molecule of a salt of neodymium in aqueous solution is united with 10 molecules of water. If the salt is the chloride or bromide, each neodymium atom has only 3 foreign atoms to disturb the periods of its electrons besides the 30 atoms in the combined water; while if the salt is the nitrate, it would have 12 foreign atoms besides those of the water. Evidently these 12 atoms would have a very much greater effect than the 3 in the case of the chloride or bromide, if we assume that the general arrangement in space is not very different in the two cases. We see, then, that the fact that the spectrum of the nitrate in aqueous solutions of considerable concentration is different from that of the chloride or bromide is what we should expect, and we also see that the

very slight change in the spectrum of the bromide and chloride on dilution, as compared with the great change in case of the nitrate, might almost have been predicted.

The change taking place with dilution is, of course, due to dissociation, each neodymium atom, after dissociation, being simply united with, say, 10 molecules of water, the anion of the molecule having left it. The neodymium ions in dilute solutions are therefore the same, no matter what salt is in solution, if we assume that the presence of the anions in the solution does not influence the hydrating power of the metallic ion. Other things being equal, therefore, we should expect that aqueous solutions of those salts whose molecules are made up of only a very few atoms united with a neodymium atom should show the least change in the spectrum when the concentration is varied, since the removal of the few atoms making up the acid radical from the hydrated molecule would in general have but a slight effect on the periods of the absorbing electrons in the metallic atom. Water solutions of salts whose molecules consist of a great many atoms united with a neodymium atom, like the nitrate, acetate, or sulphate, ought to show a considerable change in their spectra as a result of dissociation, since the removal of the great number of atoms forming the acid radical would undoubtedly have a marked influence on the periods of the absorbing electrons.

It is plain, therefore, that the simple theory outlined above furnishes a perfectly simple and rational explanation of all the phenomena which have thus far been observed in the study of the absorption spectra of neodymium salts. That it also suffices for salts of the other rare earths studied will appear in what follows.

Neodymium Nitrate in Methyl Alcohol—Beer's Law (See Plate XXI.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.80, 0.64, 0.50, 0.40, 0.32, 0.25, and 0.20, and for B they were 0.32, 0.25, 0.20, 0.16, 0.13, 0.10, and 0.08; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. in both cases.

On account of the NO_3 band the spectrum terminates at λ 3250 in the ultraviolet for A, and at about λ 3200 for B.

The absorption near λ 3500 resembles that shown by aqueous solutions much more nearly than was the case with the chloride. Only two bands appear, their positions being λ 3465 and λ 3545, respectively. The general shading extends from about λ 3450 to λ 3570.

The bands in the blue and violet are not as intense as the corresponding bands in the alcoholic solution of the chloride. In position and general character they are much more like those shown by concentrated solutions of the nitrate in water. There is a band at λ 4280, about 10 A.U. wide and not specially intense. At λ 4430 is a wide, faint band, and there is a similar one at λ 4600. Three faint bands show at λ 4690, λ 4735, and λ 4825, resembling very much the three corresponding bands in concentrated aqueous solution. The intensity here is, however, much less.

In the aqueous solution we found bands at λ 5205, λ 5225, and λ 5235. The first one was evidently due to the cation, the second, partly to the cation and partly to the molecule, while the one at λ 5235 was apparently due only to the nitrate molecule. In the methyl alcohol solution, we find only a weak shade in the region λ 5200, while at λ 5225 and λ 5240 there are two rather narrow, intense bands. There is considerable shading to both sides of these bands.

In the yellow, A shows absorption from λ 5700 to λ 5870, shading off towards the red, with a band at λ 5965. B shows a band at λ 5720, which is perhaps double; deep absorption from λ 5755 to λ 5845, with faint bands at λ 5760 and λ 5835; and a very intense band at λ 5790.

The spectrum ends near λ 7320 in a band which does not seem especially intense.

Neodymium Nitrate in Ethyl Alcohol—Beer's Law (See Plate XXII.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.32, 0.26, 0.20, 0.16,

Plate XXI.

A

B

Plate XXII.
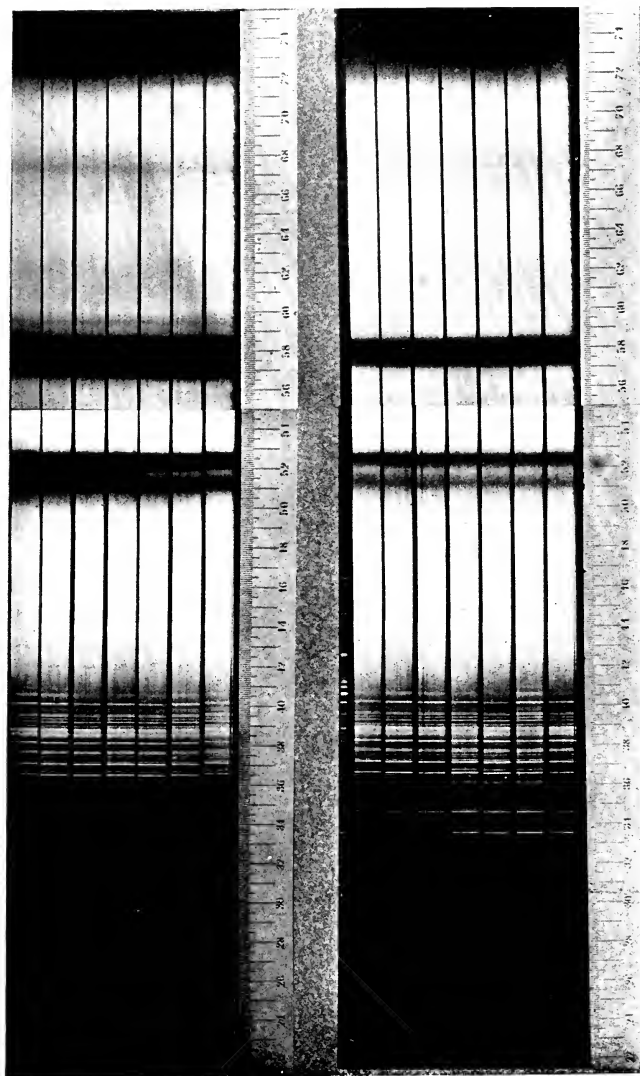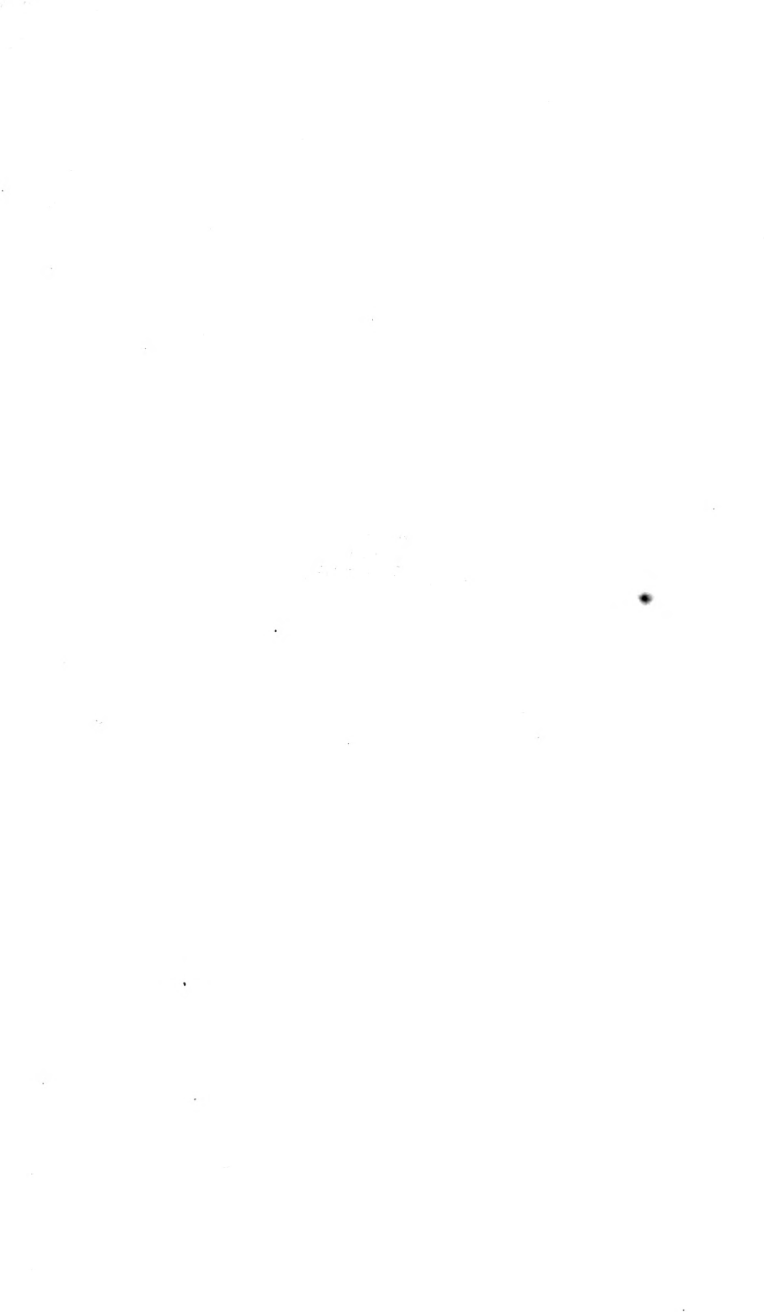
A

B

0.13, 0.10, and 0.08, and for B they were, in the same order, 0.16, 0.13, 0.10, 0.08, 0.06, 0.05, and 0.04; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm.

The solutions used in making A of this plate were of the same concentrations as those used in making B of Plate XXI., and as the depths of absorbing layer were also the same, the two plates are directly comparable.

The two spectra are very similar, but nevertheless there are some well-marked differences. The bands at λ 5225 and λ 5240, which were quite sharp and intense in the methyl alcohol solution, here show simply as one hazy band of moderate intensity, its middle being near λ 5235. Even in B, where the concentration is much less, this band does not break up into two, but simply diminishes in intensity without change of character.

The yellow group shows a wide, faint band at λ 5730 and a moderately intense band at about λ 5790, much less intense and sharp than in methyl alcohol. There is a pair of poorly-defined bands at λ 5825 and λ 5845, apparently corresponding to the band at λ 5835, observed in the solutions in methyl alcohol.

The spectrum ends at λ 7315 in a band which is not very intense or sharp. In general, the absorption in the two alcohols is about the same, the general tendency being for all absorption bands to be narrower in the methyl than in the ethyl alcohol solutions.

Praseodymium Chloride in Water—Beer's Law (See Plate XXIII.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.56, 1.92, 1.28, 0.85, 0.60, 0.42, and 0.32. For B the concentrations were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14, and 0.11, the depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm. respectively.

The solutions of praseodymium chloride are all green or yellowish-green, only the intensity of the color changing with change in the concentration.

For these solutions Beer's law holds very closely, excepting for the extreme ultraviolet absorption in A, and the yellow bands in the two or three most concentrated solutions of A.

The limits of transmission in the ultraviolet, for the most concentrated and most dilute solutions of A, are λ 2720 and λ 2650, respectively. The edge is fairly sharp, indicating the presence of a rather intense band. This is also indicated by B, where the spectrum ends abruptly at λ 2630, the limit being the same for all of the solutions.

The absorption bands shown in A are as follows: λ 4380 to 4480, strong band with red edge somewhat shaded; λ 4640 to λ 4710, sharp on red side, quite diffuse towards the violet; λ 4800 to λ 4830, sharply defined on both sides; λ 5860 to λ 5950, both edges diffuse; λ 5985, fairly narrow band with diffuse edges. The region between this band and the principal yellow one shows very strong absorption.

B shows the following: λ 4410 to λ 4465, both edges a little diffuse; λ 4685, fairly narrow band, still more diffuse towards the violet, although somewhat shaded also towards the red; λ 4815, narrow band, with edges slightly shaded; λ 5900, wide hazy band, absorption not complete, even at its middle; λ 5985, rather faint, hazy band.

The greenish tinge of the solutions would suggest that there is considerable general absorption in the red, because the absorption in the yellow is not sufficient to impart any marked color to the solution, and the bands in the violet and blue could only give it a yellow tint. The negative for A does, in fact, show pretty strong general absorption from λ 7100 to the end of the red, but no doubt a spectrophotometric study of the solutions would show general absorption much farther down into the red. The negative for B shows no sign of this absorption, for very obvious reasons.

Praseodymium Chloride in Mixtures of the Alcohols and Water (*See Plate XXIV*.).

The concentration of the praseodymium chloride was constant throughout and equal to 0.5 normal. The percentages of water in the solutions, beginning with the one whose spec-

Plate XXIII.

A

B

Plate XXIV.
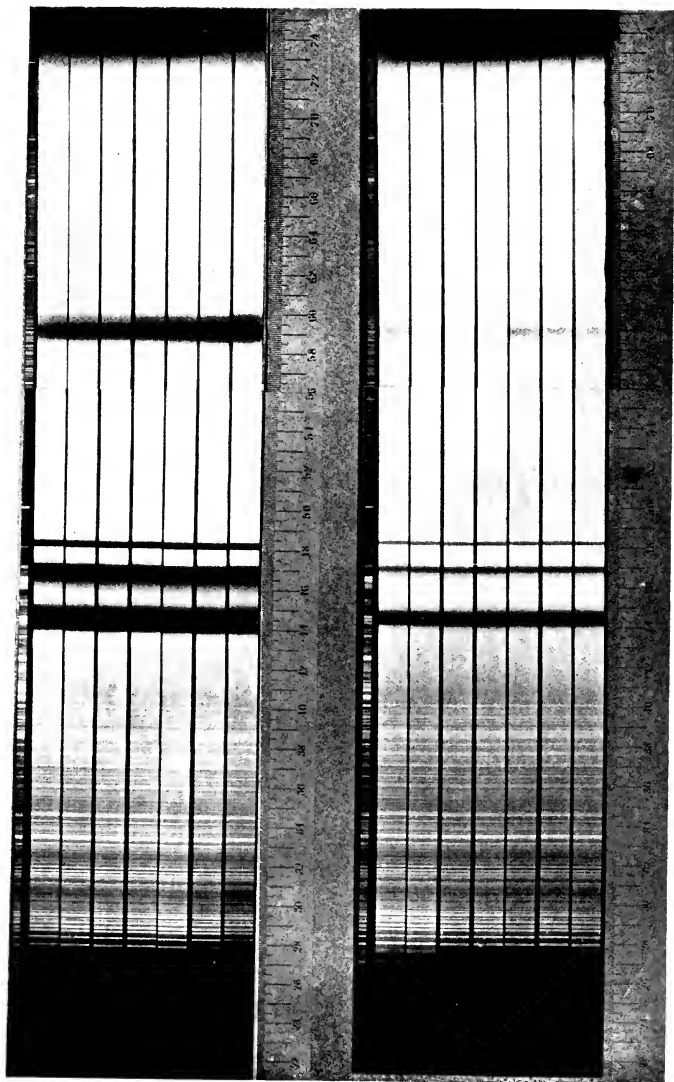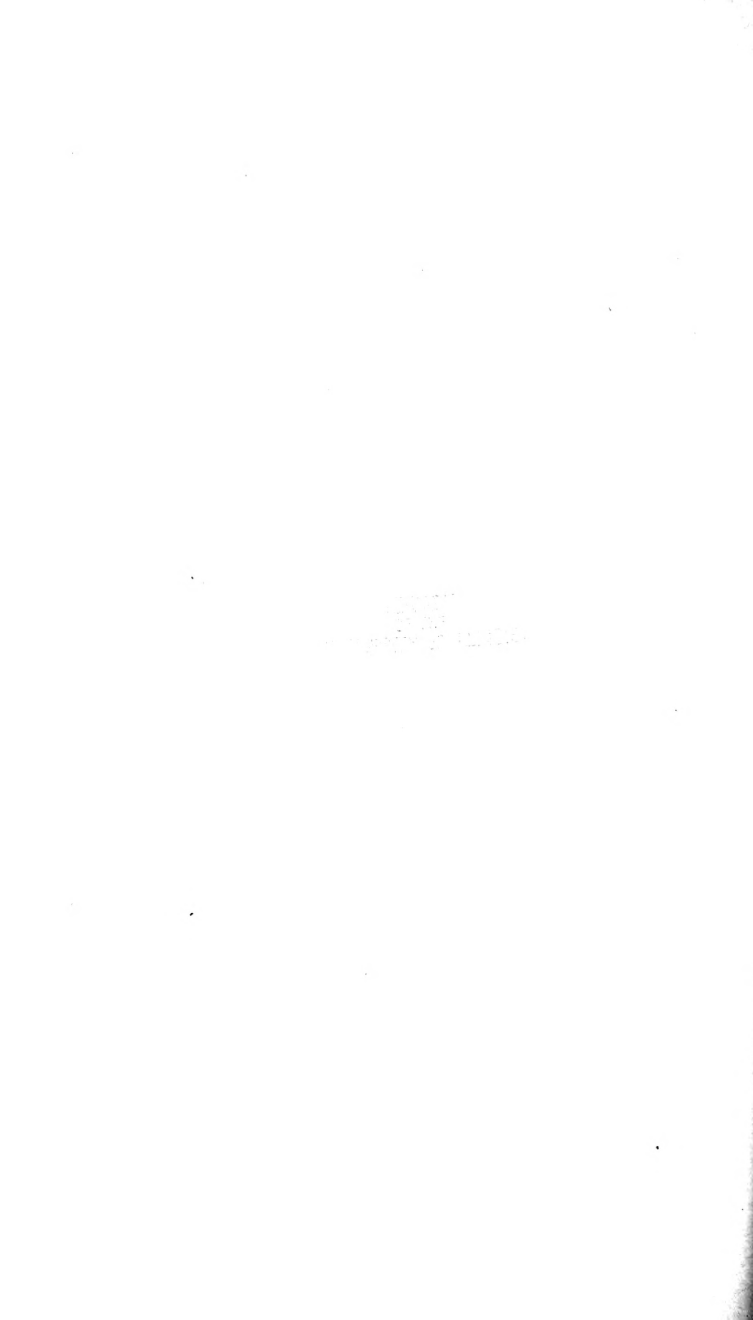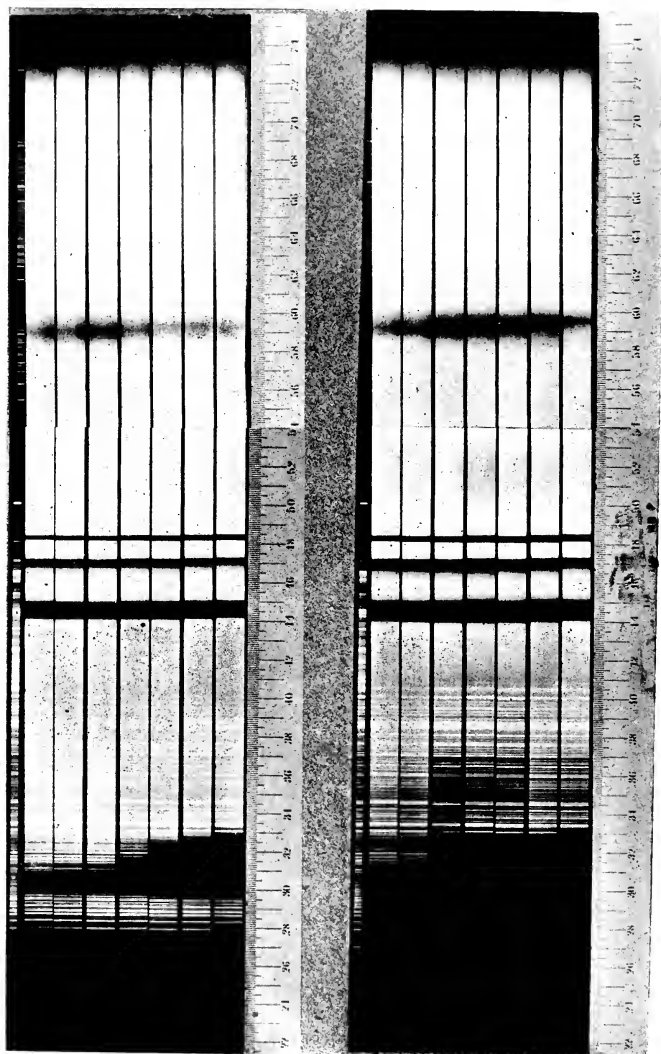
A

B

trum is adjacent to the numbered scale, were 0, 2.3, 5.6, 8, 10.6, 13.3, and 16. The depth of absorbing layer was 1.0 cm. Methyl alcohol was the chief solvent in the solutions pertaining to A, while ethyl alcohol was employed in the solutions used in making the negative for B. The two spectrograms are identical, except for a little greater general absorption in the ultraviolet with the ethyl alcohol. The most striking feature of the spectrograms is the appearance of the intense absorption band near λ 3000 as the percentage of water is gradually decreased. Only a faint trace of this band is visible with 16 per cent of water in the solution, and the band is comparatively weak even with only 8 per cent of water. From this point it increases very rapidly in width and intensity with decrease in the amount of water, until in the pure alcohol solutions its limits (transmission) are λ 2970 and λ 3230, this being by far the most intense band in the whole spectrum.

The bands in the violet and blue apparently shift somewhat towards the red, this being, due, however, to the fact that the alcohol bands are a little nearer the red end of the spectrum, and that when the percentage of water changes from 16 to 0, the two sets of bands coexist, but are far from being separated. The change is exactly the same in character as the one described in detail in discussing the λ 4760 band for neodymium chloride in mixtures of alcohol and water.

The positions of the bands in the solution containing 16 per cent of water are as follows: λ 4390 to λ 4470, λ 4660 to λ 4700, λ 4800 to λ 4825. In the solution in pure alcohol they are λ 4410 to λ 4480, λ 4690 to λ 4715, λ 4810 to 4840. Hence, it appears that the two most refrangible bands have a slightly greater width in the water solution, while the λ 4815 band is more intense in the alcoholic solutions.

The bands in the yellow show very well, indeed, the fact that here, as in the spectrum of neodymium chloride, we have the coexistence of two sets of bands when the water content of a 0.5 normal solution is in the neighborhood of 8 per cent. The band in the yellow has already been described under Beer's law, but as the concentration and depth of layer are

different here, the following will serve to indicate what the spectrum of the 16 per cent water solution shows. Absorption begins at λ 5850 and rises to a maximum at about λ 5900, then decreases to a minimum at λ 5950, from which it again rises to a maximum at about λ 5980, falling off to zero at λ 6000. The solution in pure alcohol shows the following: Weak absorption begins at λ 5800 and continues without material change up to λ 5880, where it falls almost to nothing. At λ 5900 it begins to increase and reaches a strong maximum at λ 5955, falling off gradually to zero at λ 6000. The intermediate solutions show the gradual disappearance of the bands characteristic of the aqueous solution, and the increase in intensity of those belonging to the alcoholic solution, as the percentage of water is gradually decreased. The maximum change takes place from the fifth to the third strips, counting from the numbered scale, indicating here, as with neodymium chloride, that the two sets have about half their normal intensity when the water content of the solution is about 8 per cent, or when the solution contains about 10 molecules of water per molecule of the dissolved substance.

Praseodymium Nitrate in Water—Beer's Law (See Plate XXV.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 3.2, 2.4, 1.6, 1.1, 0.75, 0.53, and 0.41. For B the concentrations were 1.1, 0.80, 0.55, 0.33, 0.26, 0.18, and 0.14; the depths of absorbing layer in both cases were 3, 4, 6, 9, 13, 18, and 24 mm.

There is a great deal of absorption in the ultraviolet, the spectrum of the most concentrated solution ending at λ 4000, while that of the four most dilute solutions of set A ends at about λ 3650. The spectra shown in B all end at λ 3570. This absorption is not to be ascribed to the NO_3 radical, as its band lies beyond λ 3300 in all the solutions thus far studied.

The absorption bands do not differ materially from those of the chloride, except that they are a trifle more intense, owing, no doubt, to the slightly greater concentration of the nitrate solutions. Also, the violet and blue bands show a

Plate XXV.

A

B
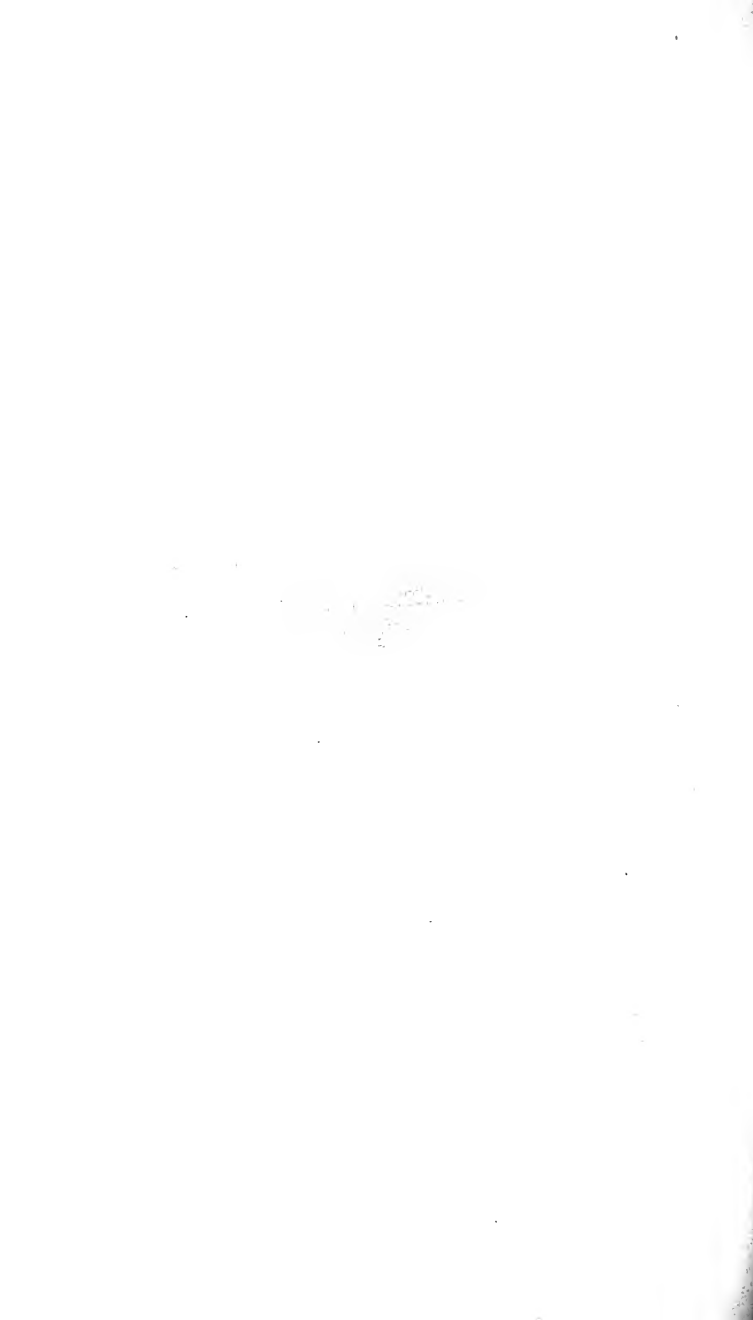
slight deviation from Beer's law in the two or three most concentrated solutions of A.

It may be said in general that the absorption spectra of the different salts of the same metal resemble each other very closely; and it is only when careful attention is paid to the structure of each individual band, or group of bands, that the differences are brought out clearly. In the process of printing and reproducing the spectrograms illustrating this section, a great deal of the finer detail has been lost, and as it is just this detail which shows the differences alluded to above, it is clear that in many cases the reproductions fail entirely to show the important points. In cases of special importance a rather full description of the appearance of the negatives has been given in the text. A full description of this nature covering all the spectrograms of the present chapter would require an amount of time and space which would be quite prohibitive and unwise.

It is hoped, however, that the plates, together with the description given in the text, will make clear the points which we have tried to emphasize most strongly, *viz.*:

1. That the absorption spectra of different salts of the same metal in the same solvent are different if the concentration is great, or, more generally, if the dissociation is only slight; and that as the dissociation becomes more and more complete, they become more and more alike.

2. That the absorption spectra of the same salt in different solvents are in general different.

3. That with change in dissociation of the salt in any one solvent, the change in the absorption spectrum of salts having anions containing only a few atoms, such as the chloride and bromide, is very slight; but that as the complexity of the anion increases, the change becomes more and more pronounced.

4. That when a salt is dissolved in mixtures of two solvents, the relative percentages of which are varied, there is not a gradual change of one spectrum into the other; but the spectrum given by the mixture is a superposition of the two spectra, the two sets of bands existing together. If the salt is one whose spectrum changes considerably with its state of dis-

sociation, we have in addition to the above phenomena the changes due to the varying dissociation of the dissolved salt produced by the varying composition of the mixture.

The explanation of these points on the working hypothesis which has guided the present work has already been given in the discussion of Plates XIX. and XX.

In the introduction to the present section the work of Helen Schaefer was referred to. It will be recalled that she studied the spectrum of the nitrate of neodymium in various solvents, and also in mixtures of two solvents, the case to which she calls special attention being mixtures in various proportions of water and acetone. She did not come to the conclusion which we have reached, that in such mixtures we have two distinct sets of absorption bands, since she considers that the bands shift gradually, some in the direction demanded by Kundt's law, and some in the opposite direction. There are two reasons why she did not draw the same conclusion that we have reached. In the first place she worked with the nitrate, which we have found shows a considerable variation in its spectrum with change in dissociation, and her solvents being water and acetone, the change in the dissociation would be very considerable. For this reason, she found a continuous change in the spectrum as more and more acetone was added, which was just what she expected. Had she worked with the chloride or bromide she would have found practically no change until the proportion of the nonaqueous solvent in the mixture had become very great, and in this event her conclusions would have been quite different.

In the second place her salts were not dehydrated (if they were, she makes no mention of the fact), and hence even in the solution in pure acetone she probably had from 6 to 10 molecules of water per molecule of the dissolved salt, which we have found will give the spectrum characteristic of the nonaqueous solvent with only about half its normal intensity. It is not very surprising, therefore, that she failed to discover the coexistence of the two sets of bands, which would have given a perfectly simple explanation of all the phenomena that she observed.

SUMMARY AND CONCLUSIONS.

It is evident from the spectra of the solutions studied in the present investigation that deviation from Beer's law is the rule rather than the exception. Of the great number of sets of solutions studied, only a very limited number appear to conform to Beer's law, and it is possible that with more exact spectrophotometric measurements this number would be reduced still further. This is exactly what we should expect, since actual solutions always contain more than one kind of "absorber," and the relative concentrations of these "absorbers" are continually changing with change in concentration of the solution. Beer's law could hold, as explained in the introductory section, only in cases where the relative concentrations of the different kinds of absorbers do not change with dilution, or where the absorption of all the different kinds of absorbers is identical. The first one of these conditions is perhaps never fulfilled, while the second one is undoubtedly approached more or less closely in certain cases, such as in aqueous solutions of neodymium chloride or bromide or of praseodymium chloride. The rule is, however, that the different absorbers have different absorbing powers, and the problem is, therefore, to decide which absorbers are responsible for the bands observed in the various spectra.

According to the theory of Ostwald, which is simply Arrhenius's dissociation theory applied to the absorption spectra of solutions, we have but two or three kinds of absorbers, namely, the molecules of the dissolved salt and one or both of the ions formed from it. In the case of all the salts studied in the present work, excepting the nitrates, the anion was colorless; so all the absorption, according to Ostwald's theory, should be due to two kinds of absorbers, the molecule and the cation. That this theory fails to account for the deviation from Beer's law observed in the ultraviolet absorption of copper salts, the red bands of cobalt salts, the ultraviolet band of cobalt chloride, and the absorption of iron chloride, has already been pointed out, for all these bands narrow with dilution, even when the number of molecules in the path of the beam of light is kept constant. Whether

this theory is able to account for the behavior of those bands which narrow with dilution when the conditions for Beer's law obtain, but which widen when molecules are kept constant, can only be decided by spectrophotometric measurements.

The work of Müller on salts of nickel and copper shows that the behavior of the red absorption band of these substances can not be accounted for on Ostwald's theory, and this makes it at least very probable that the same will be found for salts of other metals. Ostwald's theory may, therefore, be dismissed, not because it is erroneous, but because it is incomplete. It leaves out of account certain changes taking place in solutions, which produce other "absorbers" than those which it considers.

The other theories which aim to account for the deviations are of two kinds, *viz.*:

(1) Those that assume that the increased absorption in concentrated solutions is due to the formation of aggregates of the molecules of the dissolved substance, or of the molecules and the ions into which they break down on dissociation.

(2) Those that assume that the deviation is due to the formation of solvates, that is, combinations of the parts of the dissolved substance with the molecules of the solvent.

It has been shown by Hartley and other workers who have studied the change in the absorption with the change in temperature that the bands which widen with increase in concentration (conditions for Beer's law assumed to obtain) also widen with rise in temperature; that is, rise in temperature produces very much the same effect as increase in concentration. This seems to us pretty conclusive evidence against the theories which are based on the formation of aggregates, for it is well known that the change in the aggregates produced by rise in temperature is *not the same* as that produced by increase in concentration, but *exactly the opposite.*

The theories which assume the formation of solvates are not open to this objection, because it is well known that the change in the solvates produced by rise in temperature is in general the *same* as that produced by increase in concentration. As a solution becomes more concentrated the solvates

become simpler and simpler, that is, fewer molecules of the solvent are combined with each part of the dissolved substance. Rise in temperature also breaks down complex solvates into simpler ones. Of course, it does not follow that the solvates in a solution of concentration c, at temperature t, are *exactly* the same as those in a solution of concentration c_2 at a temperature t_2, since under the changed conditions it may happen that the particular solvates which were most stable when the conditions were c and t, may be less stable than solvates of nearly the same composition at c_2, t_2.

For this reason, and also because *our work on neodymium and praseodymium salts in mixed solvents seems almost conclusive evidence in favor of the existence of solvates*, we have used the solvate theory as a working hypothesis throughout this work. That it is not far from being correct is shown by the fact that all the phenomena observed in the great number of solutions studied are accounted for without anything but the simplest assumptions in regard to the behavior of the solvates in question.

We shall now summarize briefly the main points brought out in the present work.

Solutions of cobalt salts have, in general, three regions of absorption in that part of the spectrum which can be photographed without resorting to other means than the commercial dry plate. One is in the extreme ultraviolet, and we concluded that it is due to the molecules of the dissolved substance. Their absorption is influenced to some slight extent by solvation, but differently for the different salts. That no part of this absorption is due to the cobalt ions is shown by the fact that solutions of cobalt sulphate are perfectly transparent beyond λ 2200, although they are dissociated to a very considerable extent.

Another region of absorption is in the green, near λ 5200, for most solutions. This band, which is the most characteristic one of the cobalt solutions, was ascribed by Ostwald to the cobalt ion. That the molecules also absorb in this region, and in fact have a greater absorbing power than the ion, has been abundantly shown. Whether the simple theory

of dissociation is able to account for the observed deviations from Beer's law for this band is not known, but it is improbable. The question is now being investigated in this laboratory and a definite answer will probably be given in the near future.

The absorption band at λ 3300 in the spectrum of the aqueous solution of cobalt chloride, since it disappears with dilution even when molecules are kept constant, cannot be due to the cobalt chloride molecules, but we found good reasons for thinking that it is due to some hydrate of these molecules which is formed in solutions of moderate concentration even at ordinary temperature. The two bands in the same region which appear in the alcoholic solutions of the same salt behave so much like the band in the aqueous solution that they are undoubtedly due to some relatively simple alcoholate.

The bands in the red region of the spectrum of solutions of cobalt salts we concluded were due to very simple solvates, such as are formed only in the most concentrated aqueous solutions, or in solutions of moderate concentration but at very high temperatures. Donnan and Bassett assumed that these bands are due to some complex anions, such as $CoCl_2.Cl$ or $CoCl_2.Cl_2$, which would then be the same in aqueous and nonaqueous solutions. There are a great many objections to this explanation. In the first place, such complexes ought to obey the usual rule for aggregates, that is, they ought to break down with rise in temperature, whereas the change in the spectrum demands the opposite. In the second place, according to this theory the bands ought probably to be the same in aqueous as in nonaqueous solutions, which we have found is not the case. *On the theory of solvates, however, everything is perfectly clear.* The differences in the structure of the group of bands with different solvents is what we should expect, and the appearance of the bands with rise in temperature of aqueous solutions, or with the addition of large quantities of a dehydrating agent, is simply due to the formation of the required simple hydrates under these conditions.

The bands of solutions of nickel salts are all of the same type as the green cobalt band, and, hence, must be studied

spectrophotometrically. The change in the ultraviolet band with addition of dehydrating agents, however, suggests that here also hydrates play an important part. Anhydrous nickel chloride could not be dissolved in the nonaqueous solvents used, hence the work was of necessity limited to aqueous solutions.

With the exception of copper chloride in acetone, which has a band at λ 4700, all copper solutions show only two regions of absorption, one in the ultraviolet and one in the red. The ultraviolet band, since it narrows rapidly with dilution even when molecules are kept constant, cannot be accounted for on the simple theory of dissociation. And as it widens rapidly with rise in temperature, we must conclude that it is due to the solvated molecules, the absorbing power of which increases rapidly with decrease in the complexity of the solvate.

The band in the red belongs in the same class with the green cobalt band. But, as mentioned above, Müller came to the conclusion that dissociation is unable to account for its deviation from Beer's law. This also agrees with what we found in studying its behavior in mixtures of alcohol and water in the case of the chloride. Hence, we assume that solvates here also play a rôle, which, however, is not quite so apparent, owing to the fact that both the solvated ions and the molecules absorb light in this region.

Another fact which supports our view is that the absorption in the red is not widely different in different solvents, provided the concentrations are about the same; while in the ultraviolet the absorption is many times greater in the nonaqueous than in the aqueous solvents, the reason for the latter being, first, that the dissociation is much greater in aqueous than in nonaqueous solutions, and hence, for equal concentrations, the number of molecules in the latter is much greater than in the former. Secondly, the solvating power of water is much greater than that of the nonaqueous solvents used, and hence the comparatively few molecules present, by forming relatively complex hydrates, suffer a still further reduction of the absorbing power.

The only salt of iron studied was ferric chloride. It shows

only one region of absorption, namely, the one which cuts off the entire ultraviolet, and usually also the violet and blue portion of the spectrum. In aqueous solutions this absorption band narrows very rapidly with dilution, even when molecules are kept constant, indicating a marked effect of hydration. In alcoholic solutions the band remains of sensibly constant width, indicating that in this case the solvation is probably very slight. The difficulty of drawing any definite conclusions from solutions of this salt lies in the fact that the solutions are not very stable, and hence the effects may very often be masked by chemical changes of unknown amount.

Chromium salts behave very much like those of nickel. Only two of them were studied in this work and these only in aqueous solution. The behavior of their bands is quite analogous to that of the green cobalt band, and hence calls for spectrophotometric study. Their diffuse character also makes them rather unfit for spectrographic investigations.

The most interesting and important results were obtained from the study of the salts of neodymium and praseodymium, especially those of the former. These substances have not only very many absorption bands, but they are remarkably narrow and sharp, and hence peculiarly suitable for spectrographic study.

The chief experimental results were the following:

1. The absorption spectra of aqueous solutions of the chloride and bromide of neodymium change very little with change in concentration, and the two are nearly identical throughout, excepting for the fact that the absorbing power of the bromide appears to be somewhat greater than that of the chloride.

2. The absorption spectrum of aqueous solutions of neodymium nitrate is somewhat different from that of the chloride or bromide, especially if the solutions are concentrated. With decrease in concentration the spectrum changes so as to become more and more nearly identical with that of the other salts. Certain bands, therefore, increase in intensity when the conditions for Beer's law obtain. Others decrease and remain constant only when molecules are kept constant.

Examples of the first class of bands are those at λ 4275, λ 4330, and λ 5205. Examples of the second kind are the bands at λ 4282 and λ 5235.

3. Addition of large amounts of calcium or aluminium chloride to a solution of neodymium chloride does not affect the spectrum appreciably, except the shading of the yellow band, and perhaps very slightly that of the green bands.

4. Solutions of the salts in nonaqueous solvents give spectra which are not only different for different salts, but the spectrum of any one salt is different in the different solvents. The spectra of neodymium or praseodymium chloride in methyl and ethyl alcohols, which are almost exactly alike, are apparent exceptions.

5. When neodymium chloride is dissolved in mixtures of water and one of the nonaqueous solvents, and the relative amounts of the two solvents in the mixture are varied, no marked change in the spectrum is observed when the amount of water is changed from 100 per cent to about 15 or 20 per cent. As the amount of water is still further reduced we find that the solution gives a spectrum which consists of a superposition of the spectra belonging to the aqueous and the nonaqueous solutions; the former decreasing in intensity while the latter increases as the amount of water is decreased. The composition of the mixed solvent which will show the two spectra with about half their normal intensity depends upon the concentration of the salt in solution, and a constant ratio between the number of molecules of water and those of the dissolved salt was indicated by the experiments; this ratio has the value 10.

Neodymium nitrate dissolved in mixtures of water and one of the nonaqueous solvents shows exactly the same change as the chloride; but in addition we get the changes in the spectrum produced by the great change in the state of dissociation of the salt. The result is that the whole change is a much more gradual one, and hence is not nearly so striking as it is in the chloride or bromide solutions.

Praseodymium chloride dissolved in mixtures of water and methyl or ethyl alcohol shows, in general, the same kind

of change in the spectrum as neodymium chloride, but in addition there appears in the alcoholic solutions an entirely new band having no analogue in the aqueous solution. This new band in the ultraviolet is by far the most intense in the entire spectrum. It disappears entirely on the addition of water, having about half its normal intensity for a half-normal solution when the water content of the solvent is about 8 per cent.

These facts seem to us inexplicable on any other hypothesis than the one we have put forward, namely, that when a salt of one of these elements is dissolved in a solvent both the molecules of the salt and the ions formed from them become solvated, that is, they combine with a certain number of molecules of the solvent. In the case of cobalt and copper salts we found reasons for believing that a series of solvates of varying complexity was formed, while with the rare elements the spectrum points rather to the existence of only one definite solvate. A more extended study, including the changes in the spectrum produced by change in temperature, may, however, modify this conclusion somewhat.

Granting the existence of the solvates, the phenomena observed in the absorption spectra of neodymium and praseodymium admit of a perfectly natural explanation. As this explanation has already been given in full under the discussion of neodymium nitrate in water—Beer's law—we need not repeat any part of it.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
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BENZENESELENONIC ACID AND RELATED COMPOUNDS.

BY HOWARD WATERS DOUGHTY.

The work herein described was begun in the laboratory of the University of Wisconsin in 1906. As it was interrupted by the author's change of residence and considerable time has been lost on that account, it seems advisable to give an account of the work up to the present time.

Some years ago the writer was engaged in an investigation of certain aromatic sulpho acids,[1] and it seemed to him that an investigation of the analogous selenium compounds might lead to interesting results. It was decided to start with the simplest member of the series, benzeneselenonic acid, and to prepare it, if possible, by the use of benzene and selenic acid, and then to proceed to the study of the more complex acids corresponding to the sulphur compounds already mentioned.

In 1889 Chabrie[2] prepared a substance by the action of selenium tetrachloride on benzene in the presence of aluminium chloride, which he supposed was selenophenol, C_6H_5SeH. The substance crystallized in yellow needles, melting at 60°. He also tried the action of concentrated selenic acid on benzene and found that an acid was formed which gave a soluble barium salt. He did not investigate the acid further and gave no analysis of the barium salt.

Some years later Krafft and Vorster[3] showed that selenium is capable of replacing the SO_2 group in aromatic sulphones, and by means of this reaction they prepared diphenyl selenide, a colorless oil boiling at 301°–302°:

$$Se + C_6H_5.SO_2.C_6H_5 \longrightarrow$$
$$(C_6H_5.SeSO_2.C_6H_5) \longrightarrow C_6H_5.Se.C_6H_5 + SO_2.$$
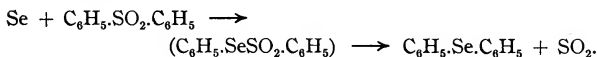
In the following year Krafft and Lyons[4] prepared selenophenol by the following method: Diphenyl selenide heated with selenium gave diphenyl diselenide, melting at 63°.5:

$$C_6H_5.Se.C_6H_5 + Se \longrightarrow C_6H_5.Se.Se.C_6H_5.$$
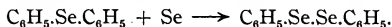
By reducing this substance with sodium and acidifying the product with sulphuric acid they obtained an oil boiling at 183°, which distilled unchanged in an atmosphere of carbon dioxide, but oxidized very rapidly in the air to diphenyl diselenide. Analysis and reactions showed the oil to be selenophenol. Evidently the substance obtained by Chabrie was diphenyl diselenide.

[1] THIS JOURNAL, **33**, 388.
[2] Bull. Soc. Chim. [2], **50**, 133; [3], **2**, 788.
[3] Ber. d. chem. Ges., **26**, 2813.
[4] *Ibid.*, **27**, 1763.

Krafft and Vorster[1] also showed that when diphenyl selenide is treated with bromine in ether solution a dibromide, $(C_6H_5)_2SeBr_2$, is obtained, which melts at 140° with decomposition. This, when treated with cold 15 per cent solution of sodium hydroxide, gives diphenylselenoxide, $C_6H_5.SeO.C_6H_5$, melting at 113°–114°, which, when treated with hydrochloric acid, forms the dichloride, $(C_6H_5)_2SeCl_2$, melting at 179°–180°. Diphenylselenoxide is also obtained directly from diphenyl selenide by oxidation with chromic acid in acetic acid solution.

Krafft and Lyons[2] also prepared diphenylselenone, $C_6H_5.SeO_2.C_6H_5$, by oxidation of diphenylselenoxide with potassium permanganate. The selenone loses oxygen when heated and yields diphenyl selenide, which forms diphenyl diselenide when heated with selenium, and diphenyl diselenide is changed by nitric acid to the nitrate of benzeneseleninic acid, $C_6H_5.SeO_2H.HNO_3$, which, when neutralized with ammonia and treated with silver (nitrate?) solution gave a crystalline precipitate of silver benzeneseleninate, $C_6H_5.SeO_2Ag$.

In 1906 Stoecker and Krafft[3] obtained a product which they describe as the hydrate of benzeneseleninic acid, $C_6H_5.SeO_2H.H_2O$, by treating diphenyl diselenide with nitric acid, precipitating the silver salt and treating it with the calculated amount of hydrochloric acid, and crystallizing the product. It melted at 122°–124°. They also prepared benzeneselenonic acid by the action of chlorine water on diphenyl diselenide, and from the silver salt they obtained what they considered to be a hydrate of the acid by precipitating the silver with hydrogen sulphide. They do not appear to have had the pure acid in hand, but prepared several of its salts. This work of Stoecker and Krafft came to my notice after the work herein recorded was well advanced, and, as the method here described is entirely different from theirs and there are certain differences in our results, it seems well to give my work in full, though not with any desire of depreciating the claims of Stoecker and Krafft to priority.

[1] *Loc. cit.*
[2] Ber. d. chem. Ges., **29,** 424.
[3] *Ibid.*, **39,** 2197.

EXPERIMENTAL.

Preparation of Selenic Acid.—The selenic acid used in this investigation was prepared from black stick selenium by the following method: The selenium was dissolved in boiling nitric acid (1:1). The solution was evaporated to dryness, the selenium dioxide dissolved in water, a little barium chloride added to remove sulphuric acid, and the solution filtered and evaporated to dryness. The selenium dioxide was then purified by sublimation, though this precaution is probably unnecessary so far as this investigation is concerned. The pure selenium dioxide was dissolved in water and a slight excess of silver nitrate solution was added. The white precipitate of silver selenite was filtered off and washed. The residue was suspended in water and an excess of bromine added. After standing overnight the silver bromide was filtered off on glass wool or asbestos and the clear dilute solution of selenic acid concentrated by evaporation in an open dish until the temperature rose to 150°. This fairly strong selenic acid was then further dehydrated by heating under diminished pressure (20 mm.) for 12 hours at 180°. The selenic acid thus obtained was perfectly clear and colorless and contained no trace of selenous acid. It had a specific gravity of 2.53.

The benzene used was anhydrous and free from thiophene. Concentrated selenic acid serves as a good test for thiophene in benzene. If thiophene is present a dark blue coloration— about the color of Prussian blue—appears at the zone of contact between the selenic acid and the benzene after standing a few minutes. If the thiophene has been removed no color appears for a long time in the cold, and then only a light brown.

Barium Benzeneselenonate.—Method I.: One hundred grams each of the selenic acid, sp. gr. 2.53, and pure benzene were placed in a 750 cc. Erlenmeyer flask connected with a return condenser, and heated continuously for 100 hours on a water bath. The contents of the flask, after heating, consisted of a layer of benzene, almost colorless and containing no appreciable amount of dissolved substance, and a heavier layer of selenic acid containing the products of the reaction. This

acid layer had about the consistency of molasses, and was dark red in color. After separating the two layers by means of a separating funnel, the acid layer was poured into an excess of barium carbonate suspended in a liter of water, and the mixture heated to boiling and filtered. The filtrate was exactly neutralized with barium hydroxide, phenolphthalein being used as indicator, and filtered again. It was then evaporated to dryness on the water bath. The solid residue was extracted by means of a Soxhlet apparatus with chloroform for several days to remove a clear syrupy substance which is one of the products of the reaction, but which has not yet been examined. The barium salt remaining was then purified by crystallization from water.

Method II.: Selenic acid, two parts, and benzene, one part, were heated in a sealed tube at 110° for 100 hours. The progress of the reaction could be watched and the equilibrium point ascertained by noting the disappearance of the benzene layer. There was pressure in the tube, doubtless due to the formation of by-products such as the one mentioned above. The acid layer was separated and the barium salt prepared as described under Method I. The product was the same in both cases.[1]

Barium benzeneselenonate crystallizes from water in small plates. If the crystals separate slowly from a cold or not too warm solution they contain 3 molecules of water. If the solution is very concentrated and near the boiling temperature the salt crystallizes with 2 molecules of water. That the water is very loosely combined is shown by the fact that the first samples, which were air-dried in the laboratory of the University of Wisconsin in midwinter, were anhydrous. The

[1] NOTE: In a preliminary report of this work, presented before the American Chemical Society in June, 1907, the statement was made that when benzene and selenic acid were heated in a sealed tube the barium salt obtained had the composition $(C_6H_5.SeO)_2Ba$. This statement was based on analyses of the salt giving the following results: Ba found, 28.69, 28.68, 28.26; calculated, 28.50. Se found, 33.58; calculated, 32.82. As it has been impossible to duplicate these results, although several attempts have been made, it seems probable that with the small quantity in hand in the first preparation there was some impurity and that the analyses were suggestive of the product $(C_6H_5SeO)_2Ba$ merely by a coincidence. In all subsequent preparations, with more perfect methods of purification, the product has always been barium benzeneselenonate.

hydrated specimens were obtained in this laboratory. It may be mentioned in passing that in Madison, Wis., in mid-winter, the air contains very little moisture, so that calcium chloride is not visibly altered by exposure to the air of the laboratory. The salt burns with explosive violence when heated so that the analyses for barium were made by precipitating barium sulphate from a solution of the salt rather than in the usual manner by igniting and treating with sulphuric acid. The selenium was determined by adding ammonium persulphate and sulphuric acid to the filtrate from the barium sulphate precipitation, and heating until the cloudiness noticed at first disappeared. Sodium bisulphite and concentrated hydrochloric acid were then added and the solution boiled until all selenium was deposited. The selenium was weighed on a Gooch filter as usual. The following results were obtained:

Of the salt deposited from a warm, fairly strong solution, 0.2343 gram lost 0.0233 gram water when heated at 110°.

	Calculated for $(C_6H_5.SeO_3)_2Ba.3H_2O$.	Found.
H_2O	9.00	9.08

Of the salt separating from a boiling concentrated solution, 0.2627 gram lost 0.0157 gram when heated to 110°.

	Calculated for $(C_6H_5.SeO_3)_2Ba.2H_2O$.	Found.
H_2O	6.19	5.98

The anhydrous salt gave results as follows:

	Calculated for $(C_6H_5.SeO_3)_2Ba$.	I.	Found. II.	III.
Ba	25.16	25.51	25.27	24.85
Se	29.01	...	...	28.53

I. was a sample of the salt with $3H_2O$; II., a sample of the salt with $2H_2O$; III. was a sample of salt prepared in the University of Wisconsin in midwinter and air-dried. It did not lose weight when heated at 110°.

Benzeneselenonic Acid.—The calculated amount of 0.1 N sulphuric acid was added to the solution of a weighed amount of the barium salt described above, and the barium sulphate was filtered off. The filtrate was evaporated to a small vol-

ume and allowed to crystallize. No difference in the product could be detected, whether the evaporation was completed in the air of the laboratory or in a vacuum desiccator over sulphuric acid. Benzeneselenonic acid separated in bunches of colorless needles, which, after drying on a porous plate, melted sharply at 142°. After cooling and solidifying the melting point was unchanged. When heated to 180° carbon dioxide and water were given off. There was no perceptible decomposition below this temperature and the beginning of decomposition appeared very sharply at this point. Benzeneselenonic acid crystallizes from aqueous solution without water of crystallization. The crystals are somewhat hygroscopic and are very easily soluble in water and in alcohol, but not in ether or benzene.

0.2654 gram gave 0.3481 gram of CO_2 and 0.0748 gram of H_2O.

	Calculated for $C_6H_5.SeO_3H$.	Found.
C	35.08	35.76
H	2.92	3.12

0.3977 gram of the acid was neutralized with 0.1 N sodium hydroxide.

	Calculated for $C_6H_5.SeO_3H$.	Found.
0.1 N NaOH	19.38 cc.	19.40 cc.

Benzeneselenonic acid gives a silver salt which is fairly soluble in water, from which it crystallizes in white, wartlike masses.

Silver Selenophenolate.—This substance is easily obtained from benzeneselenonic acid by the following method: When a solution of benzeneselenonic acid is treated with the calculated amount of silver nitrate solution no precipitate appears, but on addition of sulphur dioxide a white precipitate is formed, which immediately becomes intensely yellow, resembling cadmium sulphide in appearance. This precipitate is odorless, and is completely insoluble in water, alcohol, or ammonia. It is not changed by the action of hydrochloric acid. It dissolves in potassium cyanide. It is oxidized by nitric acid to a soluble compound, and from this solution hy-

drochloric acid precipitates silver chloride. A combustion
did not yield satisfactory results, as diphenyl diselenide dis-
tilled off, leaving the silver, and was found at the outlet of the
combustion tube, having escaped decomposition. Krafft has
mentioned the difficulty of burning diphenyl diselenide or
substances that give it when heated.

o.1850 gram of the yellow compound gave o.1007 gram of
silver chloride.

	Calculated for $C_6H_5.SeAg.$	Found.
Ag	40.91	40.92

When benzeneselenonic acid in solution is treated with re-
ducing agents, such as hydrogen sulphide, sulphur dioxide,
or, best, with zinc and hydrochloric acid, selenophenol is ob-
tained as a yellow oil with an overpowering and most nausea-
ting odor. This oil is easily extracted with ether or carbon
tetrachloride, and when the solution is evaporated the seleno-
phenol is rapidly oxidized in the air to diphenyl diselenide,
which crystallizes in pale yellow, silky needles, melting at 63°.
Krafft and Lyons give 63°.5. The odor of diphenyl diselenide
is extremely disagreeable, but is not nearly so bad as that of
selenophenol.[1]

Stoecker and Krafft[2] prepared benzeneselenonic acid by
precipitating silver from silver benzeneselenonate by means
of hydrogen sulphide and evaporating the filtrate. They
state that they obtained a hydrate of the acid in this way, but
give no melting point or analysis. From the description
which they give it would seem that their product is different
from that prepared by the method used by me.

Several attempts were made to prepare benzeneselenonyl
chloride, but without success. The action of phosphorus
pentachloride on barium benzeneselenonate is extremely
violent, being attended with flashes of light. When the phos-

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[1] The writer has already had occasion to record his experience with thiophenol
as to its physiological effects (This Journal, **33**, 393). The effect of selenophenol
on the skin is very similar to that of thiophenol, forming blisters which itch intensely.
After a time these dry up, the skin scales off, and there appears to be a deposit of red
selenium beneath it. The odor of selenophenol is very penetrating and is nauseating
beyond description.

[2] Ber. d. chem. Ges., **39**, 2197.

phorus pentachloride is used in chloroform solution the action is less violent, but the chloride was not obtained, nor was the amide obtainable by treating the reaction mixture with strong ammonia. In some experiments selenic acid was found, indicating a deep-seated change.

Benzeneseleninic Acid.—This acid was obtained by Stoecker and Krafft[1] by treating diphenyl diselenide with nitric acid. They prepared the silver salt and from that obtained what they describe as the hydrate of benzeneseleninic acid, $C_6H_5.SeO_2H$. H_2O, melting at $122°–124°$, and certainly their analysis by combustion gave values indicating this composition. Nevertheless, it appears to me that the substance as obtained by me is not a hydrate, and it seems possible that Stoecker and Krafft may have had the acid and not the hydrate.

When benzeneselenonic acid is treated with strong hydrochloric acid a white crystalline precipitate is formed and chlorine is given off. 0.3974 gram benzeneselenonic acid was dissolved in about 5 cc. water in a small distilling flask. Hydrochloric acid gas was passed through the solution and thence into a distilling flask containing potassium iodide solution. The iodine liberated was determined by titration with sodium thiosulphate. 0.2207 gram iodine was liberated, corresponding to 0.0278 gram oxygen.

	Calculated for $C_6H_5.SeO_3H \longrightarrow C_6H_5.SeO_2H.$	Found.
O	7.79	7.00

The apparatus was filled with carbon dioxide before the introduction of the hydrochloric acid and the chlorine was swept out by a current of carbon dioxide. As the results of this experiment seemed to show that benzeneselininic acid was the principal product of the reaction between hydrochloric and benzeneselenonic acids, the experiment was repeated on a larger scale. After the reaction was completed the hydrochloric acid solution was poured off from the crystalline precipitate and the latter was dissolved in chloroform and thus separated from the remaining acid solution. The chloroform solution was evaporated to dryness on the water bath, leaving a reddish

[1] *Loc. cit.*

brown oil, most of which dissolved in water and was removed from the residual tarry product by filtering. When the solution was evaporated to a small volume and allowed to cool, an almost quantitative yield of beautifully crystallized benzeneseleninic acid was obtained. This was further purified by recrystallization from water, but the difference in melting point between the first and fourth fractions was not more than half a degree. The substance was dried in the air on porous plates, and melted at 122°. Benzeneseleninic acid is much more soluble in hot water than in cold and crystallizes in very thin rhombic plates. It melts at 122°, and after cooling and solidifying, still melts at very nearly the same point. Heated to 200° it decomposes, giving off a colorless gas. As Stoecker and Krafft had obtained a product which seemed to be a hydrate of this acid and yet had approximately the same melting point, 122°–124°, especial consideration was given to this point.

0.2042 gram of the acid required 10.72 cc. of 0.1 N barium hydroxide solution for neutralization.

	Calculated for $C_6H_5.SeO_2H.H_2O$.	Calculated for $C_6H_5.SeO_2H$.	Found.
0.1 N Ba(OH)$_2$	9.86 cc.	10.80 cc.	10.72 cc.
Ba, per cent,	33.09	36.24	35.94

Stoecker and Krafft found that when their hydrate was heated for three hours under 15 mm. pressure at 100° and finally at 130° it lost 8.36 per cent in weight, while the calculated loss was 8.69 per cent. Not having a vacuum desiccator that would stand heating, I placed the acid described above in a small distilling bulb and proceeded as in distillation under diminished pressure, using a pressure of about 50 mm. and heating at a uniform temperature of 130°. The loss in weight was determined and the remaining white solid dissolved in water and titrated with 0.1 N barium hydroxide. During the heating a white sublimate was observed just above the level of the distilling bath, and some of this was even carried over into the side tube of the distilling bulb. Evidently, this would account for a loss in weight if the substance were heated in the ordinary vacuum desiccator.

0.2458 gram of acid lost 0.0130 gram when heated in the manner just described. The residue, when dissolved in water, required 12.76 cc. 0.1 N Ba(OH)$_2$ for its neutralization. Compared with the titration of the original substance without heating, this amount of acid should require 12.78 cc., so there was no diminution of acidity on heating, and the white sublimate was probably the same as the portion that did not sublime. Two explanations are possible. Either the substance is a hydrate, as claimed by Stoecker and Krafft, and yields the acid when heated, or the original substance is an acid, as shown by titration, and yields an anhydride on heating. The amount of water lost by my sample is little more than half that required by the first hypothesis.

Benzeneseleninic Anhydride.—In order to test this point portions of benzeneseleninic acid were heated at 130° in an air bath under atmospheric pressure. No constant weight could be obtained although the substance was heated for over 30 hours in the aggregate. Moreover, it was found that if it were left exposed to the air it took up very nearly as much moisture as it had lost during the heating. These facts are easily explained on the basis of the formation of an anhydride that sublimes at a temperature of about 130°. A portion of the substance that had been heated for 30 hours at 130° was dissolved in water and titrated with 0.1 N barium hydroxide. The portion originally weighed 0.1826 gram. After heating it weighed 0.1418 gram and required 7.94 cc. 0.1 N Ba(OH)$_2$ to neutralize it.

	Calculated for			
	$C_6H_5.SeO_2H.H_2O$.	$C_6H_5.SeO_2H$.	$(C_6H_5.SeO)_2O$.	Found.
0.1 N (BaOH)$_2$	6.85 cc.	7.50 cc.	7.88 cc.	7.94 cc.

A portion of the anhydride was placed while hot in a melting point tube and the tube was sealed. The substance melted sharply at 164° with no sign of decomposition, and after cooling and solidifying the melting point was unchanged.

I therefore conclude that when benzeneselenonic acid is treated with concentrated hydrochloric acid in the cold, benzeneseleninic acid is precipitated, and when this acid

crystallizes from water it does so without water of crystallization. When benzeneseleninic acid is heated at 130°, either in a vacuum or under atmospheric pressure, it forms benzeneseleninic anhydride, melting at 164°, which is not changed by heating at its melting point but decomposes at 200°. The anhydride is exceedingly hygroscopic, and if left exposed to the air it absorbs moisture, forming benzeneseleninic acid. The anhydride sublimes at about 130°.

The work on the aromatic oxygen acids of selenium will be continued in this laboratory.

AMHERST COLLEGE,
February 10, 1909.

CLXVI.—RESEARCHES ON THIOCYANATES AND ISO-THIOCYANATES: A NEW CLASS OF ISOTHIO-CYANATES. ISOTHIOCYAN ETHERS.

[EIGHTH PAPER.]

BY TREAT B. JOHNSON AND HERBERT H. GUEST.

This paper is a contribution to our knowledge of the action of potassium thiocyanate on primary alkyl halides. By the term primary halide is meant any derivative of methyl chloride, bromide, or iodide of the general formula I., in which R can represent any saturated or unsaturated organic radical:

$$R.CH_2.hal. \qquad (R)_2CH.hal. \qquad (R)_3C.hal.$$
$$\text{I.} \qquad\qquad \text{II.} \qquad\qquad \text{III.}$$
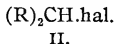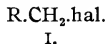
We have investigated, in this laboratory, the action of potassium thiocyanate on about eighteen different halides of this type I., besides several secondary (II.) and tertiary (III.) halides.[1] The incentive for this study was to ascertain what influence, if any, the positive or negative character of the radicals substituted for R had in determining the formation of thiocyanates and isothiocyanates. We have substituted for R in primary halides saturated and unsaturated alkyl

[1] J. Am. Chem. Soc., **23**, 283; **24**, 439, 680, 743; **28**, 1454. THIS JOURNAL, **26**, 345; **38**, 456.

and aryl groups, ester, acidamide, and diacidamide groupings, but in no case have we obtained a primary halide which reacts with potassium thiocyanate to give an isothiocyanate.

The only acyclic groups, so far as the writers are aware, which produce conditions favorable to the formation of isothiocyanates, when substituted for R in primary halides (I.), are the vinyl group $CH_2:CH$ or derivatives of this unsaturated radical. For example: allyliodide,[1] IV., and chlorallyl chloride,[2] V., react with potassium thiocyanate, giving thiocyanates

$$CH_2:CH.CH_2I \qquad\qquad CH_2:CCl.CH_2Cl$$
$$\text{IV.} \qquad\qquad\qquad \text{V.}$$
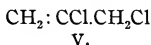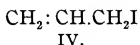
which rearrange smoothly into isothiocyanates when heated.

A careful review of the literature[3] reveals the fact that apparently the action of potassium thiocyanate on halogen substituted ethers has not been investigated.[4] As we had occasion to continue the study of the behavior of potassium thiocyanate towards alkyl halides, it seemed of interest to investigate the action of some known, primary chlormethyl ethers of the general formula $ROCH_2Cl$, in which R represents an alkyl radical, viz., CH_3, C_2H_5, etc.

We have now made the interesting observation that chlordimethyl ether,[5] VI., chlormethylethyl ether,[6] VII., and chlormethylisoamyl ether,[7] VIII., react practically quantitatively with potassium thiocyanate, giving the corresponding isothiocyanates, IX., X., and XI:

[1] Billeter: Ber. d. chem. Ges., **8**, 464. Gerlich: Ann. Chem. (Liebig), **178**, 89.

[2] Henry: Ber. d. chem. Ges., **5**, 188.

[3] Beilstein's Handbuch.

[4] Sommelet (Compt. rend., **143**, 827) and Gauthier (*Ibid.*, **143**, 831) have recently shown that the chlormethyl ethers react smoothly with mercuric, silver, and cuprous cyanides, giving the corresponding nitriles, $ROCH_2.CN$. They also combine smoothly with the alkali salts of organic acids, giving compounds of pharmaceutical value. [Patent (No. 137585) der Farbenfabriken vorm. Friedr. Bayer und Co., "Darstellung der Salicylsäurealkyloxymethylester aus Chlormethylalkyläthern und Salicylaten." This compound, $o\text{-}HO.C_6H_4.CO_2.CH_2OCH_3$, is used as an antirheumatic. Wedekind: Ber. d. chem. Ges., **36**, 1383.]

[5] Friedel: Bull. Soc. Chim., **28**, 171. Kleber: Ann. Chem. (Liebig), **246**, 97. Henry: Bull. Acad. Roy. Belgique [3], **25**, 439; Ber. d. chem. Ges., **26**, Ref. 933. Favre: Bull. Soc. Chim. [3], **11**, 879; Compt. rend., **119**, 284.

[6] de Gaspari: Gazz. chim. ital., **27**, II., 297.

[7] Favre: *Loc. cit.*

$$CH_3OCH_2Cl \qquad C_2H_5OCH_2Cl \qquad C_5H_{11}OCH_2Cl$$
$$\text{VI.} \qquad\qquad \text{VII.} \qquad\qquad \text{VIII.}$$

$$\downarrow \qquad\qquad\qquad \downarrow \qquad\qquad\qquad \downarrow$$

$$CH_3OCH_2NCS \qquad C_2H_5OCH_2NCS \qquad C_5H_{11}OCH_2NCS$$
$$\text{IX.} \qquad\qquad \text{X.} \qquad\qquad \text{XI.}$$
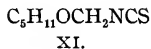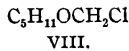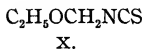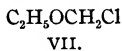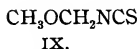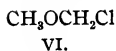
The isothiocyanate structure is established by the facts that these compounds are desulphurized by warming with an alkaline solution of lead acetate, and react with thiobenzoic acid with formation of carbon bisulphide. They also combine smoothly with ammonia and organic bases, giving derivatives of a new class of thioureas—$R'NHCSNHCH_2OR$.

Our observation that the primary chlormethyl ethers react with potassium thiocyanate, giving isothiocyanates, is in accord with the experimental evidence which has been brought forward in previous papers from this laboratory.[1] The results do not conform to the theory[2] that a strong, negative character favors the formation of isothiocyanates. The benzoyl—C_6H_5CO—and carbethoxy—$COOC_2H_5$—radicals have a more negative influence than methoxy (—OCH_3), nevertheless their substitution in primary halides[3] produces a condition which is unfavorable for the formation of isothiocyanates.

$$CH_3.CH_2Cl \qquad CH_3O.CH_2Cl \qquad C_2H_5OOC.CH_2Cl \qquad C_6H_5CO.CH_2Cl$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad\qquad \downarrow \qquad\qquad\qquad \downarrow$$

$$CH_3CH_2.SCN \quad CH_3OCH_2.NCS \quad C_2H_5OOCCH_2SCN \quad C_6H_5COCH_2SCN$$
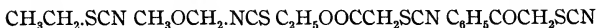
Previous results[4] have indicated that possibly an unsaturated condition, as well as a negative character, is required for the formation of isothiocyanates. The facts that the saturated radicals, *viz.*, methoxy-, ethoxy-, and isoamoxy-, and the unsaturated vinyl group $CH_2:CH$ produce conditions favorable for the formation of isothiocyanates show that the idea of the influence of unsaturated condition of the molecule is not

[1] *Loc. cit.*

[2] Michael: J. prakt. Chem., **37**, 509 (1888). Dixon: J. Chem. Soc., **75**, 390 (1889).

[3] Aripides: Ann. Chem. (Liebig), **249**, 10; Obaegia: *Ibid.*, **266**, 326; Dyckerhoff : Ber. d. chem. Ges., **10**, 120.

[4] *Loc. cit.*

of wide application. A similar unsaturated condition exists in benzyl chloride, XII., as in allyl iodide, XIII., but the former gives a thiocyanate,[1] while the latter forms an isothiocyanate.[2]

$$CH_2Cl \qquad \qquad \begin{matrix} CH_2I \\ | \\ C \\ H \diagup \diagdown CH_2 \end{matrix} \qquad \qquad \begin{matrix} CH_2.Cl \\ | \\ O.CH_3 \end{matrix}$$
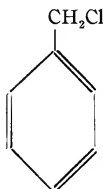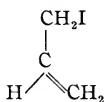
XII.   XIII.   XIV.

The etherthioureas, XV., which are formed by the action of the isothiocyan ethers on amines, are well crystallized compounds and stable at ordinary temperature. They are derivatives of the unknown oxymethylthiourea, XVI. The corresponding oxygen compound, oxymethylurea, XVII., has recently been prepared by Einhorn and Hamburger[3] by condensing formaldehyde with urea in presence of barium hydroxide. Some characteristic transformations of this new class of thioureas, XV., will receive attention in a later publication.

$$\begin{matrix} NHCH_2OR \\ | \\ CS \\ | \\ NHR' \end{matrix} \qquad \begin{matrix} NHCH_2OH \\ | \\ CS \\ | \\ NH_2 \end{matrix} \qquad \begin{matrix} NH.CH_2OH \\ | \\ CO \\ | \\ NH_2 \end{matrix}$$
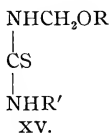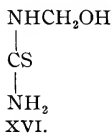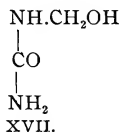
XV.   XVI.   XVII.

EXPERIMENTAL PART.

Isothiocyandimethyl Ether, $CH_3.OCH_2NCS$.—Fifty-two grams of chlordimethyl ether, dissolved in 100 cc. of anhydrous benzene, were digested with 75 grams of dry potassium thiocyanate, at 110°, for two days. After being filtered from potassium chloride and potassium thiocyanate, and freed from the excess of benzene at 120°–130°, the isothiocyanate was

[1] Ber. d. chem. Ges., **2**, 637; **5**, 689.
[2] *Loc. cit.*
[3] Ber. d. chem. Ges., **41**, 24.

purified by distillation under diminished pressure. It boiled at 56°–60° at 30 mm. and at 138° at 770 mm. The isothiocyanate is a colorless oil which has an irritating odor and attacks the eyes. Analysis (Kjeldahl):

	Calculated for C_8H_5ONS.	Found.
N	13.5	13.13

Isothiocyanmethylethyl Ether, $CH_3CH_2OCH_2NCS$.—This compound was prepared by digesting chlormethylethyl ether in benzene with potassium thiocyanate for about 40 hours at 120°–130°. It boiled at 93°–97° at 97–100 mm. pressure. The yield was excellent. The isothiocyanate is a colorless oil, which has an unpleasant odor and attacks the eyes, producing tears. It is very stable at ordinary temperature, and underwent no change after preservation for five months. It reacts with thiobenzoic acid at 100° with evolution of carbon bisulphide.

Analysis (Kjeldahl):

	Calculated for C_4H_7ONS.	Found.
N	11.96	11.55

Isothiocyanmethylisoamyl Ether, $C_5H_{11}.O.CH_2.NCS$.—This isothiocyanate was prepared under the same conditions as the two preceding isothiocyanates. From 140 grams of the chlormethylisoamyl ether we obtained 100 grams of the isothiocyanate boiling at 111°–114° at 22–23 mm. pressure. It boiled, under ordinary pressure, at 208°–210°, and at 122°–125° at 34 mm. pressure. This isothiocyanate appears to be less stable than the corresponding methyl and ethyl derivatives and slowly deposits a yellow substance on long exposure to the air.

Analysis:

0.0981 gram of substance gave 7.4 cc. N at 19°.5 and 773 mm.

	Calculated for $C_7H_{13}ONS$.	Found.
N	8.81	8.80

Behavior of Isothiocyanmethylisoamyl Ether towards Thiobenzoic Acid.—About 6.0 grams of the isothiocyanate and the

calculated proportion of thiobenzoic acid were dissolved in benzene, and the solution heated for several hours on the steam bath.

The excess of benzene was then distilled off and mixed with an alcoholic solution of potassium hydroxide and some copper sulphate. We obtained at once a heavy, yellow precipitate of copper xanthate, indicating the presence of carbon bisulphide. The product of the reaction was a heavy, viscous oil which finally deposited about 0.1 gram of yellow, crystalline material on long standing. This substance was insoluble in an aqueous solution of sodium hydroxide and contained sulphur. It crystallized from 95 per cent alcohol in prismatic crystals which melted at $160°–161°$ to an oil without effervescence. A nitrogen determination (Kjeldahl) agreed with the calculated value for a polymeric form of *isothiocyanmethyl-isoamyl ether*, $(C_5H_{11}.O.CH_2.NCS)_x$.

	Calculated for $(C_7H_{13}ONS)_x$.	Found.
N	8.81	8.92

Ethoxymethylthiourea, $C_2H_5.O.CH_2NHCSNH_2$.—Some isothiocyanmethylethyl ether was poured into an excess of strong, aqueous ammonia and the mixture shaken vigorously until the isothiocyanate completely dissolved. The solution was then heated on the steam bath, in a good draught, to remove the ammonia and water as quickly as possible. We obtained a viscous, hydroscopic oil which immediately solidified on cooling. After washing with ether the thiourea melted at $92°–93°$ to a clear oil. The compound is very soluble in water and alcohol and apparently undergoes decomposition by protracted heating with these solvents. It crystallized from benzene in plates.

Analysis (Kjeldahl):

	Calculated for $C_4H_{10}ON_2S$.	Found.
N	20.9	21.5

1-Phenyl-2-ethoxymethylthiourea, $C_6H_5NHCSNHCH_2OC_2H_5$.— This thiourea was prepared by dissolving 3.0 grams of isothiocyanmethylethyl ether in anhydrous ether and then adding

the calculated amount of aniline (2.4 grams). Reaction took place with evolution of heat, causing the ether to boil, and the thiourea separated in colorless crystals. It is very soluble in hot ethyl alcohol but deposits, on cooling, in six-sided plates, or tabular crystals, melting at 125°–126° to a clear oil.

Analysis:

0.1320 gram substance gave 15 cc. N at 21° and 772 mm.

	Calculated for $C_{10}H_{14}ON_2S$.	Found.
N	13.33	13.14

1-Paratolyl-2-ethoxymethylthiourea,

$CH_3C_6H_4NHCSNHCH_2OC_2H_5$.—A quantitative yield of this thiourea was obtained when 4.5 grams of *p*-toluidine were dissolved in ether with 5.0 grams of isothiocyanmethylethyl ether. It crystallized from ethyl alcohol in plates melting at 120° to an oil.

Analysis (Kjeldahl):

	Calculated for $C_{11}H_{16}ON_2S$.	Found.
N	12.50	12.49

Action of Aqueous Ammonia on 1-Paratolyl-2-ethoxymethyl-thiourea.—Two grams of the thiourea and about 8–10 cc. of strong, aqueous ammonia were heated at 140°–150° for 2 hours. There was some pressure when the tube was opened and a clear, colorless solution was obtained. After concentration of this solution, and cooling, we obtained a good yield of material in glistening plates. They melted at 41°–42° and were soluble in dilute acids and insoluble in alkalis. The compound was identified as *p*-toluidine. A mixture of the substance and pure *p*-toluidine melted at 42°–43°.

1-Phenyl-2-isoamoxymethylthiourea,

$C_6H_5NH.CSNHCH_2OC_5H_{11}$. — From isothiocyanmethylisoamyl ether and aniline. It is extremely soluble in warm isoamyl alcohol but separates, on cooling, in rhombic plates melting at 109° to an oil.

Analysis (Kjeldahl):

	Calculated for $C_{13}H_{20}ON_2S$.	Found.
N	11.11	10.96

1-Paratolyl-2-isoamoxymethylthiourea,

$CH_3.C_6H_4NHCSNHCH_2OC_5H_{11}$.—A quantitative yield of this thiourea was obtained when *p*-toluidine and isothiocyan-methylisoamyl ether, in molecular proportions, were dissolved in ether. It crystallized from isoamyl alcohol in plates melting at 119°.

Analysis (Kjeldahl):

	Calculated for $C_{14}H_{22}ON_2S$.	Found.
N	10.53	10.40

Action of Aqueous Ammonia on 1-Paratolyl-2-isoamoxy-methylthiourea.—When this thiourea was heated with aqueous ammonia at 140°–150° it was decomposed with formation of *p*-toluidine melting at 42°.

1,1-Methylphenyl-2-isoamoxymethylthiourea,

$(CH_3) (C_6H_5)N.CSNHCH_2OC_5H_{11}$.—Prepared from isothiocyan-methylisoamyl ether and monomethylaniline. It crystallized from isoamyl alcohol in stout, well-developed prisms melting at 87°.

Analysis (Kjeldahl):

	Calculated for $C_{14}H_{22}ON_2S$.	Found.
N	10.53	10.13

New Haven, Conn.,
January 18, 1909.

NOTE ON SOLUBILITY DETERMINATIONS WITH THE REFRACTOMETER.

By Frederick H. Getman and F. B. Wilson.

In a recent paper on the "Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer,"[1] Osaka shows that the relation between the angles of refraction of a mixture and its components may be simply expressed by the equation

$$ax + bx^2 = \delta - \delta_1 = \Delta,$$

where δ and δ_1 represent the angles directly observed on the

[1] Memoirs College Sci. Eng., Kyoto Imperial Univ., **1**, 265 (1906–7).

divided circle of the refractometer when a solvent and solution are examined, x the quantity of solute in grams per 100 cc. or 100 grams of solution, and a and b constants.

Solving this equation for x we have

$$x = -\frac{a}{2b} \pm \sqrt{\frac{\frac{a^2}{4b} - \Delta}{b}} \qquad (1),$$

where the lower sign is taken if a and b have opposite signs.

The author claims that this empirical formula is more convenient and reliable than the well-known relation

$$100(n - 1)/d = p_1(n_1 - 1)/d_1 + p_2(n_2 - 1)/d_2,$$

where n and d denote the index of refraction and density of a mixture and $n_1, n_2, \ldots \ldots$ and $d_1, d_2, \ldots \ldots$ the corresponding magnitudes of the components whose percentage amounts are $p_1, p_2, \ldots \ldots$

In his paper the author applies the formula to solutions of benzophenone in alcohol, potassium chloride in water, and ethyl ether in water. In each of these cases the agreement between observed and calculated values is good for the more concentrated solutions but the percentage error increases rapidly with the dilution.

In concluding his paper Osaka emphasizes the simplicity and convenience of the method and calls attention to the fact that it can be used for solubility determinations where ordinary methods fail.

Having at hand considerable data from a recent study of the refractive indices of aqueous solutions[1] it seemed of interest to us to further test the validity of Osaka's formula and at the same time to compare it with an equation expressing the concentration of a solution as a simple linear function of its index of refraction.

If the refractive indices of a series of solutions of the same solute are plotted against the corresponding concentrations it is found that the points so obtained all lie approximately on the same straight line. If N_w denotes the refractive index

[1] THIS JOURNAL, **40**, 468 (1908).

of the solvent at the same temperature as that at which the index of the solution is measured and N_s denotes the refractive index of the solution containing x grams of solute in 100 cc. of the solution, then

$$x = \frac{N_s - N_w}{\alpha} \qquad (2),$$

where α is the constant of the straight line equation.

In the accompanying tables the following notation is used:

x = number of grams of solute in 100 cc. of solution,
δ = observed angle on divided circle of refractometer,
N_s = index of refraction of solution for sodium light,
x_1 = concentration of solution calculated by formula (1),
x_2 = concentration of solution calculated by formula (2),
a and b = constants in formula (1),
α = constant in formula (2).

Table I.—*Potassium Chloride.* $t = 20°.7$.

$a = 0.284$ $b = 0.0019$ $\alpha = 0.001260$

x.	δ.	N_s.	x_1.	x_2.
20	62°20′	1.35764	...	...
16	63°13′	1.35301	15.89	15.81
10	64°35′	1.34603	...	...
6	65°36′	1.34096	6.07	6.26
2	66°32′	1.33648	2.60	2.68

Table II.—*Potassium Bromide.* $t = 21°.9$.

$a = 0.248$ $b = 0.0012$ $\alpha = 0.001120$

x.	δ.	N_s.	x_1.	x_2.
40	58°52′	1.37655	42.6	38.8
30	60°45′	1.36613	30.8	29.5
20	62°46′	1.35536	...	...
15	63°48′	1.35000	...	...
8	65°21′	1.34221	8.0	8.14
6	65°50′	1.33984	6.26	6.02
4	66°18′	1.33759	3.9	4.01
3	66°30′	1.33663	3.1	3.15

Table III.—Potassium Iodide. $t = 20°.5$.

$a = 0.275$ $b = 0.000883$ $\alpha = 0.001265$

x.	δ.	N_s.	x_1.	x_2.
80	49°30′	1.42155	88.12	77.83
40	57°40′	1.38334	. . .	. . .
30	59°48′	1.37134	. . .	. . .
16	63° 8′	1.35344	14.32	16.08
15	63°20′	1.35241	13.42	15.27
8	65° 5′	1.34353	6.72	8.25
6	65°37′	1.34090	4.62	6.17
3	66°23′	1.33719	1.82	3.24

Table IV.—Potassium Nitrate. $t = 20°.7$.

$a = 0.204$ $b = 0.0016$ $\alpha = 0.000876$

x.	δ.	N_s.	x_1.	x_2.
20	63°43′	1.35043	20.67	19.79
15	64°33′	1.34619	. . .	. . .
10	65°22′	1.34187	. . .	. . .
6	66° 7′	1.33850	5.91	6.22
4	66°25′	1.33705	4.22	4.52
3	66°37′	1.33608	3.18	3.41
2	66°48′	1.33521	2.26	2.42
1	67°	1.33426	1.25	1.33

Table V.—Potassium Chloride. $t = 20°.1$.

$a = 0.2375$ $b = 0.0125$ $\alpha = 0.000914$

x.	δ.	N_s.	x_1.	x_2.
6	66°10′	1.33823	7.53	5.26
5	66°21′	1.33735	5.23	4.66
4	66°30′	1.33663	. . . .	. . . .
3	66°39′	1.33592	. . . .	. . . .
2	66°50′	1.33505	1.98	2.14
1.5	66°55′	1.33465	1.51	1.70
1	67°	1.33426	1.12	1.28

Table VI.—*Potassium Chromate.*　$t = 19°.8$.

$a = 0.442$	$b = 0.0041$		$\alpha = 0.002012$	
x.	δ.	N_s.	x_1.	x_2.
40	$53°25'$	1.40811	46.23	37.28
30	$56°19'$	1.39110	37.98	28.83
20	$59°30'$	1.37301	...	...
15	$61°14'$	1.36351	...	...
8	$63°50'$	1.34983	8.30	8.32
6	$64°37'$	1.34586	6.17	6.34
4	$65°28'$	1.34163	4.10	4.24
3	$65°52'$	1.33968	3.10	3.27

Table VII.—*Cane Sugar.*　$t = 24°.5$.

$a = 0.3018$	$b = 0.000917$		$\alpha = 0.001424$	
x.	δ.	N_s.	x_1.	x_2.
40	$56°32'$	1.38985	40.51	39.86
30	$59° 1'$	1.37572	...	...
20	$61°35'$	1.36163	...	...
10	$64°21'$	1.34736	9.96	10.02
7.09	$65°10'$	1.34311	7.02	7.04
4	$66° 4'$	1.33871	4.06	3.95
3.55	$66°15'$	1.33783	3.36	3.34
1.42	$66°52'$	1.33489	1.28	1.26
0.57	$67° 7'$	1.33371	0.48	0.44

　　Inspection of the data recorded in the preceding tables shows that the refractometric method for solubility determination gives at best only approximate results.

　　The observation of Osaka that the percentage error is greatest in the more dilute solutions is confirmed.

　　This failure of the formula with dilute solutions is probably to be attributed to the preponderating influence of the solvent on the optical properties of the solution.

　　A comparison of the results obtained by formulas (1) and (2) shows that the latter is quite as satisfactory as the former.

　　Furthermore formula (2) is not empirical and involves less laborious calculations.

AMERICAN

CHEMICAL JOURNAL

PHENOLTETRACHLORPHTHALEIN AND SOME OF ITS DERIVATIVES.[1]

By W. R. Orndorff and John A. Black.

The series of compounds formed by heating phthalic anhydride with phenols, and known as the phthaleins, were discovered by ' von Baeyer[2] in 1871. The reaction between phthalic anhydride and phenol he formulated as follows:

$$C_8H_4O_3 + 2C_6H_6O = C_{20}H_{14}O_4 + H_2O;$$
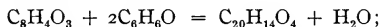
regarding phenolphthalein as analogously constituted to oxyanthraquinone:

$$C_6H_4{<}^{COC_6H_4OH}_{COC_6H_4OH} \qquad C_6H_4{<}^{CO}_{CO}{>}C_6H_3OH.$$

$$\text{Phenolphthalein.} \qquad \text{Oxyanthraquinone.}$$
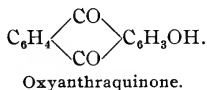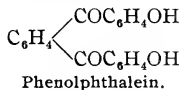
Later, in 1880,[3] Baeyer and his coworkers established the constitution of phenolphthalein by showing that it could be made synthetically from diphenylphthalid, previously obtained by Friedel and Crafts by treating phthalyl chloride

[1] Read at the Baltimore meeting of the American Chemical Society.
[2] Ber. d. chem. Ges., **4,** 659.
[3] Ann. Chem. (Liebig), **202,** 36.

with benzene in the presence of aluminium chloride and called by them phthalophenone. Baeyer first showed that this substance did not have the structure

$$C_6H_4 \diagup \begin{matrix} COC_6H_5 \\ COC_6H_5 \end{matrix}$$
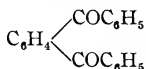
assigned to it by its discoverers, but that it was a diphenyl derivative of phthalid,

$$C_6H_4 \diagup \begin{matrix} CH_2 \\ CO \end{matrix} \diagdown O,$$

and had the constitution

$$C_6H_4 \diagup \begin{matrix} C(C_6H_5)_2 \\ CO \end{matrix} \diagdown O,$$
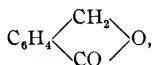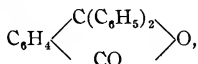
since on reduction in alkaline solution with zinc dust it gave triphenylmethanecarboxylic acid,

$$(C_6H_5)_2CHC_6H_4COOH,$$
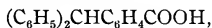
which, when heated with barium hydroxide, splits up into triphenylmethane and carbon dioxide.

By converting this diphenylphthalid into dinitrodiphenyl-phthalid by the action of nitric acid, reducing to diaminodiphenylphthalid by means of tin and hydrochloric acid, and treating the diaminodiphenylphthalid in acid solution with nitrous acid he obtained a dioxydiphenylphthalid. This dioxydiphenylphthalid was found to be identical with phenolphthalein, which must therefore have the structure

$$C_6H_4 \diagup \begin{matrix} C(C_6H_4OH)_2 \\ CO \end{matrix} \diagdown O \quad \text{or} \quad (C_6H_4OH)_2C \diagup \begin{matrix} C_6H_4CO \\ \end{matrix} \diagdown O.$$
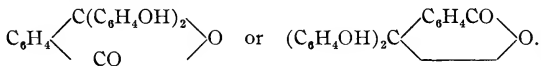
Hence, in the formation of the phthalein from phthalic anhydride it is not the anhydride oxygen which is replaced by the two phenol residues, as first supposed by Baeyer, but one of the other two oxygen atoms, as shown in the equation

$$C_6H_4 \diagup \begin{matrix} C O \\ CO \end{matrix} \diagdown O + \begin{matrix} H \, C_6H_4OH \\ H \, C_6H_4OH \end{matrix} = C_6H_4 \diagup \begin{matrix} C(C_6H_4OH)_2 \\ CO \end{matrix} \diagdown O + H_2O.$$
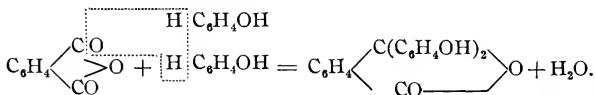
As to the position of the hydroxyl groups with reference to the methane carbon atom, Baeyer considers it quite likely that they are in the para position, since phenols in which the para position is already occupied, such as *p*-chlorphenol and *p*-cresol, do not give phthaleins but derivatives of fluoran,

Fluoran.
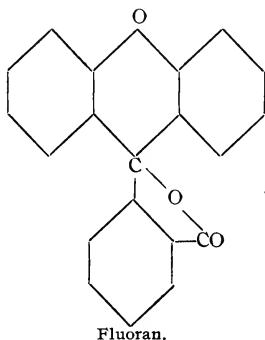
The formation of *p*-dioxybenzophenone when phenolphthalein is fused with caustic alkalies,

$$C_6H_4 \underset{CO}{\overset{C(C_6H_4OH)_2}{\diagdown}} O + KOH =$$

$$C_6H_5COOK + CO \underset{C_6H_4OH(p)}{\overset{C_6H_4OH(p)}{\diagdown}},$$
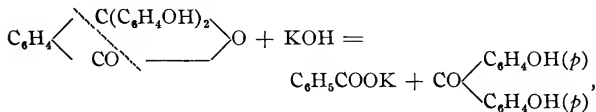
is a further proof of the para position of the hydroxyl groups in phenolphthalein.

Baeyer calls attention to the very characteristic color change which takes place when phenolphthalein is dissolved in a solution of an alkali, and states that the violet color of the salts of phenolphthalein shows the close connection of these salts to fuchsine and aurine, as expressed in the following formulas:

$$(C_6H_4NH_2)_2C \overset{C_6H_4}{\underset{}{\diagup}} NH_2Cl, \qquad (C_6H_4OH)_2C \overset{C_6H_4}{\underset{}{\diagup}} O,$$

Fuchsine. Aurine.

$$(C_6H_4OH)_2C \overset{C_6H_4CO}{\underset{}{\diagup}} O.$$
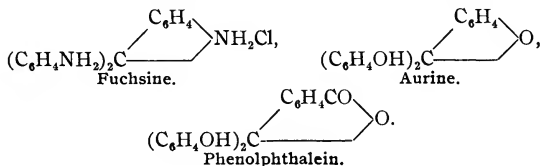
Phenolphthalein.

In 1892 A. Bernthsen[1] put forward the idea that the color-less phenolphthalein has the lactone structure (I.) while the violet-red salts have the quinoid formula (II.):

$$C_6H_4-C\underset{OC-----O}{\overset{C_6H_4OH}{\diagdown}}\overset{C_6H_4OH}{C_6H_4OH}, \qquad C_6H_4C\underset{COOH}{\overset{C_6H_4OH}{\diagdown}}C_6H_4=O.$$
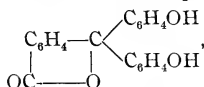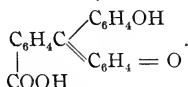
I. Phenolphthalein   II. Phenolphthalein in its salts
(colorless).   (colored).

Since the publication of this paper much work has been done on the constitution of the phthaleins and their salts and it may be said that the above view is now generally accepted by chemists. The phthaleins are regarded as tautomeric substances yielding two classes of derivatives, colorless compounds having the lactoid formula (I.) and colored substances to which the quinoid structure (II.) is assigned.

Recently Green and King[2] have published the results of their work on the constitution of the phthalein salts, which seem to establish the above view on a firm basis. They have succeeded in preparing not only the colored, quinoid esters of phenolphthalein (I.) and of quinolphthalein, but also those of their monomethyl (II.) and dimethyl ethers:
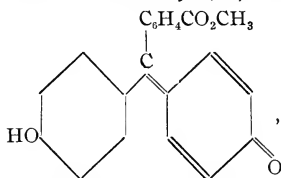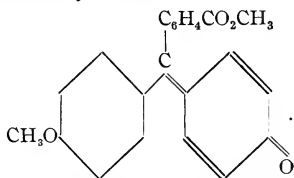
I. Methyl ester of phenol-   II. Methyl ester of phenolphthalein
phthalein.   methyl ether.

These esters all possess a deep color, ranging from orange to red. They are of a high degree of instability, being saponi-fied not only by the weakest alkalies but even by water alone. Since they were made by the ordinary method of esterifica-tion and so readily undergo saponification they must have the structure given above.

[1] Chem. Ztg., **104**, 1956.
[2] Ber. d. chem. Ges., **39**, 2365 (1906), and J. Soc. Chem. Ind., **27**, 4 (1908).

Further proof of the quinoid structure of the salts of phenol-phthalein is given by the work of R. Meyer and Marx.[1] They prepared the colored ether ester (II.) of tetrabromphenol-phthalein from the blue disilver salt (I.) by treating it with ethyl iodide:
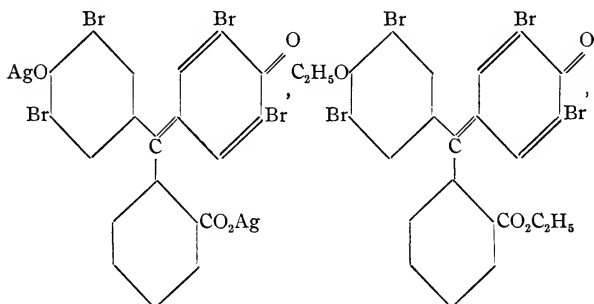
I. Disilver salt of tetrabromphenol-phthalein.

II. Colored ether ester of tetra-bromphenolphthalein.
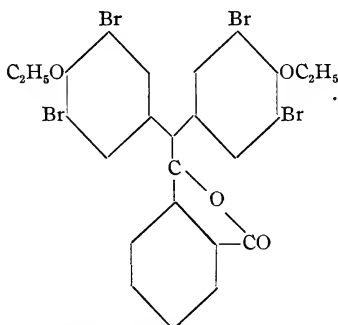
III. Colorless diethyl ether of tetrabromphenolphthalein.

They found it impossible to obtain the colored ether ester pure, however, as it is partially converted into the colorless lactoid diethyl ether (III.) with the greatest ease on recrys-

[1] Ber. d. chem. Ges., **40**, 1437 (1907).

tallization from various solvents. Later R. Meyer and Marx[1] prepared the red alkali salts of phenolphthalein by treating the alkali solution with an excess of the phthalein, filtering off the undissolved material, and evaporating the solution to dryness on the water bath. Analyses gave results agreeing with the formulas $C_{20}H_{12}O_4K_2$ and $C_{20}H_{12}O_4Na_2$. From the dry potassium salt (I.) they made the yellow colored quinoid ether ester (II.) by suspending it in dry benzene and heating with an excess of ethyl bromide.
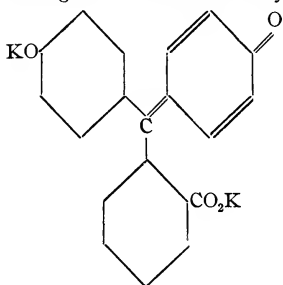
I. Red dipotassium salt of phenolphthalein.
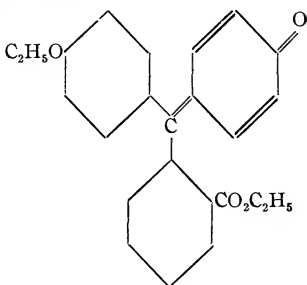
II. Yellow diethyl ether ester of phenolphthalein.

This ether ester also goes over into the colorless lactoid diethyl ether (III.) on recrystallization from solvents.
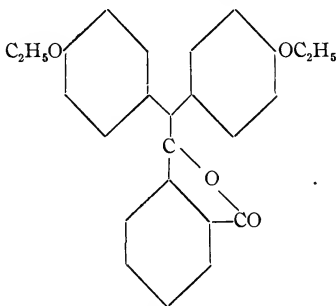
III. Colorless diethyl ether of phenolphthalein.

[1] Ber. d. chem. Ges., **40,** 3603 (1907) and **41,** 2446 (1908).

Still further confirmation of the quinoid formula for the salts of phenolphthalein is afforded by the work of K. Meyer and Hantzsch.[1] They have prepared red double salts of phenolphthalein, of the colored methyl ester, and of the colorless dimethyl ether, with aluminium chloride and with stannic chloride. They represent the structure of the compounds with stannic chloride as follows:

$$\text{HOC}_6\text{H}_4 \diagdown\diagup \text{Cl}_3\text{SnO}_2\text{CC}_6\text{H}_4 \diagup \text{C} = \langle\!\langle \;\; \rangle\!\rangle = \text{O} \diagup\diagdown \overset{H}{\underset{Cl}{}},$$
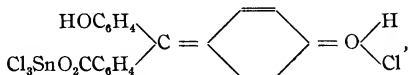
Red double salt with phenolphthalein.

$$\text{HOC}_6\text{H}_4 \diagdown\diagup \text{CH}_3\text{O}_2\text{CC}_6\text{H}_4 \diagup \text{C} = \langle\!\langle \;\; \rangle\!\rangle = \text{O} \diagup\diagdown \overset{SnCl_3}{\underset{Cl}{}},$$
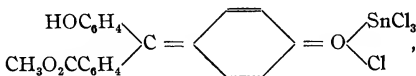
Red double salt with the methyl ester of phenolphthalein.

$$\text{CH}_3\text{OC}_6\text{H}_4 \diagdown\diagup \text{Cl}_3\text{SnO}_2\text{CC}_6\text{H}_4 \diagup \text{C} = \langle\!\langle \;\; \rangle\!\rangle = \text{O} \diagup\diagdown \overset{CH_3}{\underset{Cl}{}}.$$
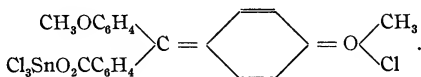
Red double salt with the colorless dimethyl ether of phenolphthalein.

In 1887 Graebe,[2] in connection with his investigation of tetrachlorphthalic acid, made tetrachlorfluorescein and tetrachlorgallein and their acetates. He states that tetrachlorphthalic anhydride combines with phenol in exactly the same way as phthalic anhydride, but gives no details of the method for making phenoltetrachlorphthalein nor did he prepare any of its derivatives.

The present investigation was undertaken for the following reasons:

(1) To ascertain the conditions under which phenoltetrachlorphthalein and its derivatives can best be made, and

(2) To study the effect of the introduction of negative or acid groups into the molecule of phenolphthalein.

[1] Ber. d. chem. Ges., **40**, 3479 (1907).
[2] Ann. Chem. (Liebig), **238**, 318.

It was thought that by introducing chlorine into the phthalic acid residue in the place of the four hydrogen atoms or by making the tetrabrom or tetraiodo derivative of this phenoltetra-chlorphthalein it would be possible, owing to the acidifying influence of the halogens, to obtain a colored quinoid compound. A. Classen and W. Löb[1] have apparently made a similar compound, a hydrate of tetraiodophenolphthalein, by acidifying a strongly alkaline solution of the tetraiodophthalein, cooled to —5°, with hydrochloric acid, also cooled below 0°. The hydrate separates as a *yellowish brown* precipitate. This was filtered off, dried, dissolved in chloroform, and precipitated with ligroin. Analyses showed that it differed from the tetraiodophthalein precipitated from alkaline solution at ordinary temperatures by one molecule of water. This compound Classen and Löb designate as tetraiodophenolphthalein carbinolcarboxylic acid,
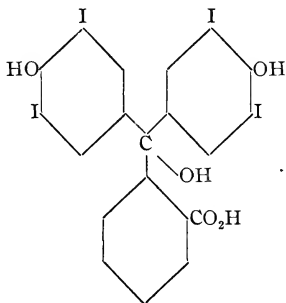
It differs from the tetraiodophthalein not only by one molecule of water, but also in that it is easily soluble in chloroform and ether. It is converted into tetraiodophenolphthalein by the loss of a molecule of water when it is heated to 100°.

As the carbinolcarboxylic acid would be a *colorless* compound according to Baeyer,[2] it is very probable that this hydrate is a quinoid form of the phthalein and has one of the two fol-

[1] Ber. d. chem. Ges., **28**, 1606 (1895).
[2] Ann. Chem. (Liebig), **354**, 152.

lowing structures, according as the water is regarded as water of constitution (I.) or water of crystallization (II.):

I.   II.
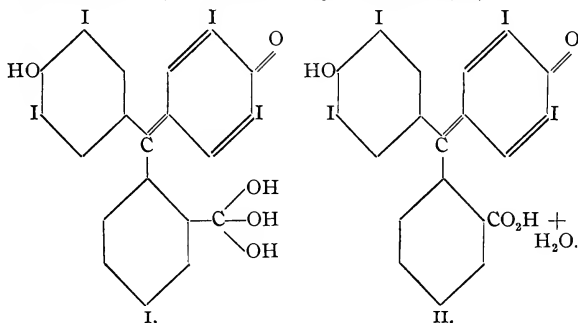
As the substance may be dissolved in chloroform and precipitated by ligroin without undergoing any change, the first formula seems the more probable one. Compounds similar to this tetraiodophenolphthalein hydrate are also known. Fluorescein hydrate, eosin hydrate, dinitrofluorescein hydrate, and tetranitrofluorescein hydrate[1] are all well-known colored compounds differing from the corresponding phthaleins by one molecule of water, and hence they must be represented by formulas similar to the above.

It was also thought that the introduction of four atoms of chlorine into the phthalic acid residue might, in accordance with the ester rule of Victor Meyer, prevent the formation of the lactone ring, that is, the formation of an inner *ester*. Meyer found that substituted benzoic acids in which the substituents occupied the two ortho positions to the carboxyl group do not form esters or form them only with great difficulty by the catalytic method of esterification. Now in phenoltetrachlorphthalein both the ortho positions to the carboxyl group are occupied, and hence it ought not to form an ester very readily and might possibly not form the inner ester, *i. e.*, the lactone,

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[1] As tetranitrofluorescein hydrate has a pinkish white color, according to Hewit and Perkins (J. Chem. Soc., **77**, 1330) it is probable that it is a mixture of the *colored* hydrate and the *colorless* carbinolcarboxylic acid.
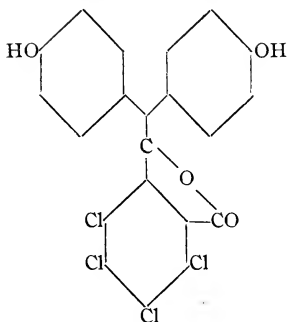
Phenoltetrachlorphthalein (lactone form).

In this connection it may be mentioned that Osorowitz[1] found that tetrachlordioxyfluorescein and dichlordioxy-fluorescein do not yield esters with sulphuric acid and alcohol, while dibromdioxyfluorescein does. He calls attention to the fact that in the first two compounds both ortho positions are occupied, while in the dibromdioxyfluorescein they are not; in other words, the conduct of these compounds is in accordance with the Victor Meyer rule.

It seemed likely, therefore, that phenoltetrachlorphthalein would be a colored quinoid compound,
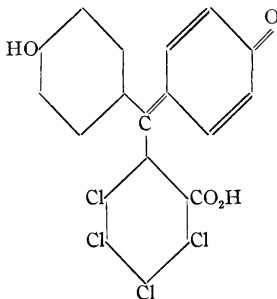
Phenoltetrachlorphthalein (quinoid form)

[1] Ber. d. chem. Ges., **36**, 1083.

more especially since both tetrachlorfluorescein and tetra-
chlorgallein, which have been prepared by Graebe, are col-
ored. It also seemed probable that phenoltetrachlorphthalein
would prove to be a much stronger acid than phenolphthalein
itself and that, unlike phenolphthalein, it would not be sensi-
tive to carbonic acid. In this case it could be used as an in-
dicator in alkalimetry and acidimetry in place of phenol-
phthalein and methyl orange.

EXPERIMENTAL.

Materials.—The phenol used in this investigation was
Kahlbaum's pure crystallized product. This was subjected
to distillation, the first fraction rejected, and only the product
distilling between 180°–181° made use of. This product,
after solidifying, was perfectly white and melted sharply at
42°.

The tetrachlorphthalic anhydride was prepared from the
commercial product (Kahlbaum's). It contained both the
acid and the anhydride and was quite pure. It was first con-
verted into the sodium salt, by boiling with a strong solution
of sodium hydroxide, and the tetrachlorphthalic acid pre-
cipitated from the hot solution by adding an excess of hydro-
chloric acid. When the solution was cold, the acid was fil-
tered off, washed with cold water, and again crystallized
from hot water. This method of purification gave pure tetra-
chlorphthalic acid, melting at 255°–257° (corrected), as had been
previously shown by Dr. Delbridge in this laboratory by very
careful analyses in connection with his work on tetrachlor-
phthalic acid.[1] The tetrachlorphthalic acid was then converted
into the anhydride by heating it in a water oven at a tempera-
ture of about 100° for one hundred and twenty hours, pre-
vious work having shown this to be a sufficient time for its
complete conversion into the anhydride. The change into
the anhydride can be brought about in a shorter time at a
higher temperature but with a loss of some of the anhydride,
which sublimes very readily at temperatures above 100°. The
zinc chloride used as a condensing agent was the C. P. article.
It was freshly fused and powdered just before being used.

[1] THIS JOURNAL, **41**, 393.

The sulphuric acid was also the C. P. article, 98.7 per cent, specific gravity 1.8406.

Pure fuming sulphuric acid containing 15 per cent free sulphur trioxide was also used.

Method.—The condensing agents used by Baeyer in making phenolphthalein from phenol and phthalic anhydride were fused zinc chloride, anhydrous stannic chloride, and concentrated sulphuric acid. Experiments in which all three of these substances were used separately showed that at 120° (the temperature employed by Baeyer in making phenolphthalein) only a very small yield of phenoltetrachlorphthalein was obtained. Using zinc chloride and a higher temperature the yield was not only small but the product was extremely dark in color. Stannic chloride is open to the objection that it is quite expensive, difficult to remove from the reaction products, and, as it boils at 120°, at which temperature only a small amount of tetrachlorphthalein is formed, it could not be used at a higher temperature. After many trials with concentrated sulphuric acid, specific gravity 1.8406, and with fuming sulphuric acid containing 15 per cent free sulphur trioxide, it was found that, taking into consideration the purity of the product and the yield of the phenoltetrachlorphthalein, the latter was the best condensing agent. The proportions of materials finally adopted were 100 grams of tetrachlorphthalic anhydride, 100 grams of fuming sulphuric acid containing 15 per cent of free sulphur trioxide, and 200 grams of phenol. These materials were placed in a 500 cc. round-bottomed flask, closed by a cork carrying a thermometer, and a small glass tube to act as an air condenser. The flask was then immersed in a sulphuric acid bath and heated at a temperature of 145°–150° for about 12 hours until the dark brown liquid solidified. After cooling, the flask was broken, the product separated from the broken glass, transferred to a 2-liter round-bottomed flask, and distilled with steam until the distillate ceased to give a test for phenol with bromine water. The material remaining in the flask was repeatedly boiled with water to remove any unchanged tetrachlorphthalic acid, sulphuric acid, and other soluble products. The residue was

then heated with dilute sodium hydroxide solution, which dissolved the phthalein with a red color, and the solution was separated by filtration from the tetrachlorfluoran formed as a by-product. The phenoltetrachlorphthalein was then precipitated from the filtrate with an excess of hydrochloric acid, boiled with water, filtered off on a Buchner funnel, and washed free from chlorides with hot water. This process also removed any unchanged tetrachlorphthalic anhydride which might have been present in the crude phthalein. Obtained in this way the product had a faint pink color. The average yield was 65 per cent of the calculated, that is, 65 grams of the 100 of tetrachlorphthalic anhydride used were converted into phenoltetrachlorphthalein. Tetrachlorfluoran was always formed as a by-product of the reaction, about 15 grams being obtained from 100 grams of the tetrachlorphthalic anhydride. This corresponds to a conversion of about 10 grams of the tetrachlorphthalic anhydride into tetrachlorfluoran. Of the original 100 grams of anhydride used, therefore, 65 grams were converted into phenoltetrachlorphthalein, 10 grams into tetrachlorfluoran, and 25 grams either remained uncombined or were converted into sulphonic acids of phenoltetrachlorphthalein.

Ethyl alcohol (95 per cent) and absolute methyl alcohol proved to be the best solvents for purifying the product, and repeated crystallization and boiling with bone black were necessary in order to obtain an absolutely white phenoltetrachlorphthalein. The air-dried product thus recrystallized from alcohol contains no alcohol or water of crystallization. Chlorine determinations on this product by the lime method resulted as follows:[1]

	Weight of substance, gram.	Weight of silver chloride, gram.	Chlorine, per cent.
I.	0.1866	0.2364	31.32
II.	0.1876	0.2362	31.13
	Calculated for $C_{20}H_{10}Cl_4O_4$,		31.11

The substance is therefore a tetrachlor substitution product of phenolphthalein.

Properties of the Phenoltetrachlorphthalein.—The phenol-

[1] International atomic weights (1908) are used in this paper.

tetrachlorphthalein resembles phenolphthalein very closely in all its properties. It is very soluble in hot alcohol, from which it crystallizes in crystal crusts. The crystals from methyl alcohol have been examined by Professor A. C. Gill of the Mineralogical Department of Cornell University, who reports as follows:

"The best crystals, obtained from solution in methyl alcohol, are nearly rectangular, colorless plates, reaching 0.5 mm. in length and about 0.2 to 0.3 mm. in breadth, with a thickness not exceeding 0.1 mm., usually about 0.05 mm. They are probably monoclinic, the large faces being the clinopinacoid, the other bounding surfaces being the base and a prism of about 54°. The angle β, as measured on the microscope stage, is approximately 93°. The extinction angle is 21° to 22°, greater optical elasticity making this angle with the vertical axis in acute β. The axial ratio $a:b = 0.51:1$. The double refraction is rather strong, giving interference colors of the higher orders in the thicker crystals.

"Since Groth found phenolphthalein to be triclinic, these crystals were carefully examined for any characteristics that might indicate that symmetry; but no divergence from parallelism in extinction could be observed when the plates were viewed through their edges, nor was any appearance of twinning detected. All evidence, therefore, is in favor of true monoclinic crystallization."

The alcoholic solution becomes milky on the addition of water and, after standing for some time, the phenoltetrachlorphthalein separates in fine needles similar to those formed when an excess of acid is added to a hot alkaline solution of the phthalein. Methyl and ethyl alcohols, acetone, ether, and glacial acetic acid dissolve the phthalein readily, while it is only slightly soluble in chloroform, benzene, and carbon bisulphide. The amorphous phthalein obtained by precipitation from a cold alkaline solution with an acid seems to be more readily soluble than the crystallized variety. In water the phenoltetrachlorphthalein is less soluble than phenolphthalein and even on boiling with water for a long time but little, if any, goes into solution. When boiled with water in soft-

glass vessels the solution takes on a faint pink color due to the solution of some of the alkali from the glass and the formation of an alkaline salt.

In concentrated sulphuric acid the phthalein dissolves readily in the cold with a reddish yellow color, probably owing to the formation of a sulphate,

,
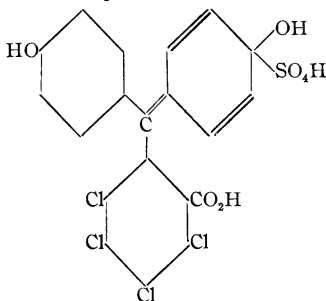
and it is precipitated unchanged from this solution by water. When the substance is heated with concentrated sulphuric acid to 120° or allowed to stand with it for 12 hours, it dissolves with the same reddish yellow color but is no longer precipitated by water, probably owing to the formation of a sulphonic acid, as this aqueous solution gives the same color changes with alkalies as the phthalein itself.

Phenoltetrachlorphthalein does not melt even when heated to 300°.

Salts of Phenoltetrachlorphthalein.—Phenoltetrachlorphthalein, like phenolphthalein, is a very weak acid and does not give well characterized salts. In the caustic alkalies or in the alkaline carbonates it dissolves very readily, forming colored solutions of the alkaline salts. In concentrated solutions the color is red, in thin layers purple, while in dilute solutions it is violet-red. In very dilute alkaline solutions the color has a bluish tint which distinguishes it from phenolphthalein.

The addition of a large excess of the caustic alkalies to the dilute alkaline solution of the phthalein decolorizes it on

standing, probably owing to the formation of the tripotassium
or sodium salt of the carbinolcarboxylic acid,

$$C_6Cl_4\Big\langle{}^{C(OH)(C_6H_4OK)_2}_{COOK}\,.$$
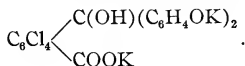
The addition of acids to the violet-red alkaline solution de-
colorizes it at once and precipitates the phthalein, as it is
practically insoluble in water. The phenoltetrachlorphthalein
may therefore be used as an indicator in acidimetry and alka-
limetry in the same way as phenolphthalein. Indeed we
have found that for titrating organic acids it is better than
phenolphthalein as the end point is sharper, and although it
is sensitive to carbon dioxide, it is not so much so as phenol-
phthalein. It cannot be used as an indicator for titrating
alkaline carbonates or alkalies in the presence of alkaline car-
bonates except by boiling off the carbon dioxide. An alkaline
solution is not decolorized so readily by alcohol as a correspond-
ing solution of phenolphthalein, as the following experiment
made for us by Dr. T. G. Delbridge shows:

A. *Phenolphthalein* (mol.
wt. 318).—Dissolved 0.0032
gram in 10 cc. of alcohol, di-
luted to 100 cc. with distilled
water, and added 2.5 cc. of
N/100 sodium hydroxide solu-
tion.

Color, light red, decidedly
lighter than B.

Added alcohol until the
solution was completely de-
colorized. Required 10 cc.
of alcohol.

2 cc. of N/100 sodium hy-
droxide solution were then
added to the colorless solu-
tion.

Color, light red.

B. *Phenoltetrachlorphthal-
ein* (mol. wt. 456).—Dis-
solved 0.0046 gram in 10 cc.
of alcohol, diluted to 100 cc.
with distilled water, and added
2.5 cc. of N/100 sodium hy-
droxide solution.

Color, deep red, decidedly
deeper than A.

Added alcohol until the
solution was completely de-
colorized. Required 30 cc.
of alcohol.

2 cc. of N/100 sodium hy-
droxide solution were then
added to the colorless solu-
tion.

Color, reddish purple.

The alcohol used was 94 per cent by volume and was distilled from sodium hydroxide previous to being used to remove acids. The distilled water was boiled to remove carbon dioxide. Phenoltetrachlorphthalein is therefore preferable to phenolphthalein as an indicator for titrating alcoholic solutions. No salt is precipitated from an alkaline solution by alcohol nor was it possible to precipitate a sodium salt by treating a solution of sodium ethylate in alcohol with an excess of the phthalein dissolved in alcohol. Ammonia dissolves the phthalein with the same color as the caustic alkalies. On boiling this solution the ammonia is driven off and the color gradually becomes fainter and finally disappears, the phthalein being reprecipitated. The free phthalein does not form an ammonium salt when placed in a desiccator over a concentrated solution of ammonia, nor when treated with dry ammonia gas. Calcium hydroxide and barium hydroxide solutions also dissolve the phthalein with a red color.

The disodium salt was made by dissolving 4.56 grams of the phthalein in alcohol, adding a solution of exactly 0.46 gram of sodium in alcohol, and evaporating to dryness on the water bath. The red disodium salt thus obtained dissolves in water or alcohol with a red color. In dilute aqueous solution it undergoes hydrolysis to a considerable extent, especially when the solution is boiled, as is shown by the precipitation of phenoltetrachlorphthalein and the fact that the solution loses almost all its color.

An attempt was made to prepare double salts of the tetrachlorphthalein with stannic and aluminium chlorides according to the method of K. Meyer and Hantzsch. It was dissolved in nitrobenzene and treated with the calculated quantity of aluminium chloride or anhydrous stannic chloride, also dissolved in nitrobenzene. When this mixture was poured into carbon disulphide, nothing but unchanged phenoltetrachlorphthalein was precipitated. Unlike phenolphthalein, therefore, the phenoltetrachlorphthalein does not form double salts with either stannic or aluminium chlorides. It also does not combine with hydrochloric acid gas to form a hydrochloride.

Attempts to make a monomethyl ester or a monomethyl

ester. hydrochloride according to the method of Green and
King, by dissolving the phthalein in absolute methyl alcohol
saturated with zinc chloride or containing 100 per cent sul-
phuric acid and passing in dry hydrochloric acid gas, were un-
successful.   Neither the methyl ester nor the hydrochloride
of the ester could be isolated, although, judging from the
deep red color of the solution, they may have been formed.
This is in conformity with the ester rule of Victor Meyer.
The converse of the Meyer rule, that esters of diortho substi-
tuted acids are not saponified at all or only with great diffi-
culty, does not seem to hold here.   Phenoltetrachlorphthalein
must have the structure of a lactone, since it is a colorless
compound and gives a colorless diacetate and a colorless
dimethyl ether.   That is, it is an *inner ester*, as shown in the
formula

$$C_6Cl_4 \diagup_{CO}^{C(C_6H_4OH)_2} \!\!\!\searrow O,$$
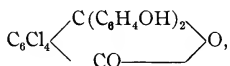
and yet the slightest trace of even the weakest base is suffi-
cient to break up this lactone ring (saponify the inner ester),
and give a salt of the phthalein

$$C_6Cl_4 \diagup_{COOK}^{C \diagup^{C_6H_4OH}_{\diagdown C_6H_4}} = O.$$
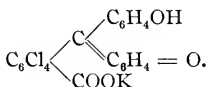
Phenoltetrachlorphthalein, like phenolphthalein, acts as a
mild purgative.   The physiological action is being investi-
gated by Professor J. J. Abel, of the Johns Hopkins Univer-
sity.[1]

Tetrachlorfluoran.—This substance is analogous in every
respect to fluoran and is formed in a similar manner as a by-
product in the preparation of phenoltetrachlorphthalein.   As
in the case of the formation of fluoran the phthalic acid residue
here enters the two phenol molecules in the ortho positions to
the hydroxyl groups and at the same time the two phenol
hydroxyl groups lose a molecule of water:

Tetrachlorfluoran.
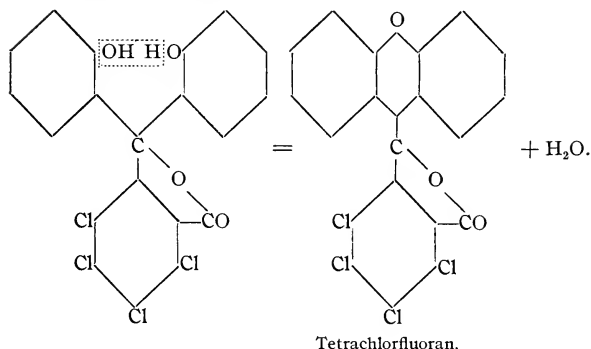
The average yield of the tetrachlorfluoran was 15 grams from the 100 grams of tetrachlorphthalic anhydride used.

The crude product, separated from the phenoltetrachlorphthalein, was boiled with dilute sodium hydroxide solution, filtered, washed thoroughly with hot water till the wash water ran through colorless, and again boiled with dilute sodium hydroxide solution. This process was repeated as long as the material imparted any color to the alkaline solution, *i. e.*, as long as it contained any phenoltetrachlorphthalein. It was then filtered off, washed, dried, and crystallized from benzene, bone black being used to decolorize the benzene solution. After filtering off the bone black and evaporating some of the benzene, colorless crystals of the tetrachlorfluoran separated. These were filtered off, washed with benzene, dried in the air, and analyzed, a modification of the lime method which had been found to be of great value in the investigation of tetrachlorgallein being used. This modification consists in heating the substance with lime in the usual way, dissolving the mass in dilute nitric acid in an Erlenmeyer flask, adding a measured excess of standard silver nitrate solution, closing the flask with a rubber stopper, and shaking the contents vigorously for a few minutes. The silver chloride, mixed with the carbonaceous material and insoluble

matter from the lime, is then filtered off and thoroughly washed, and the excess of silver nitrate in the filtrate determined with a standard solution of ammonium sulphocyanate, ammonium ferric sulphate being used as an indicator. The standard silver nitrate solution used was exactly tenth-normal, that is, 1 cc. was equivalent to 0.003545 gram of chlorine. This method of determining chlorine is very accurate and rapid and was used in most of the analyses. The results of the analyses of tetrachlorfluoran were as follows:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.1812	16.53	32.34
II.	0.1926	17.58	32.36
	Calculated for $C_{20}H_8Cl_4O_3$,		32.38

Tetrachlorfluoran is soluble in alcohol, benzene, and glacial acetic acid from which solutions it may be obtained in crystals. The crystals from benzene were examined by Professor Gill, who reports as follows:

"The stout, colorless, prismatic crystals are probably triclinic. They are optically biaxial, with *very* strong double refraction and an extinction angle which reaches about 35° as a maximum."

Tetrachlorfluoran is not acted upon by aqueous solutions of the caustic alkalies even on boiling. It dissolves in a concentrated solution of alcoholic caustic potash, probably forming a salt of the carbinolcarboxylic acid,

We attempted to prepare an ester or an ester hydrochloride of this carbinolcarboxylic acid by the method of Green and King. These authors prepared the hydrochloride (I.) and red methyl ester hydrochloride (II.) of quinolphthalein, to which they assign the formulas

I.

$$C\text{—}C_6H_4CO_2H$$

HO OH

O

Cl

II.

$$C\text{—}C_6H_4CO_2CH_3$$

HO OH

O

Cl

representing them as having the orthoquinoid structure and as oxonium salts. It seemed possible, if the above formulas are correct, that we might obtain a methyl ester hydrochloride of tetrachlorfluoran having the structure

O—Cl

C

Cl CO₂CH₃

Cl Cl

Cl
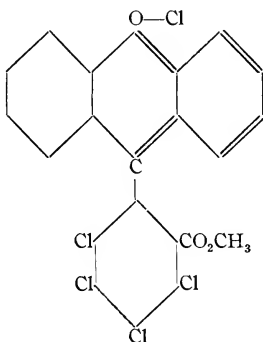
Five grams of the tetrachlorfluoran were dissolved in absolute methyl alcohol, a saturated methyl alcoholic solution

of zinc chloride was added, and dry hydrochloric acid gas then passed into the boiling alcoholic solution for four hours. No change in color took place. The alcohol was then evaporated and the residue treated with water. Unchanged tetrachlorfluoran was recovered. No reaction had taken place.

In another attempt the tetrachlorfluoran was dissolved in concentrated sulphuric acid, the solution diluted with absolute methyl alcohol, and dry hydrochloric acid gas passed into the boiling mixture for four hours. It was thought that the oxonium sulphate (I.) would be formed first and that this would give the ester sulphate or chloride (II.):

$+ CH_3OH + HCl =$

I.

$+ H_2SO_4 + H_2O.$

II.
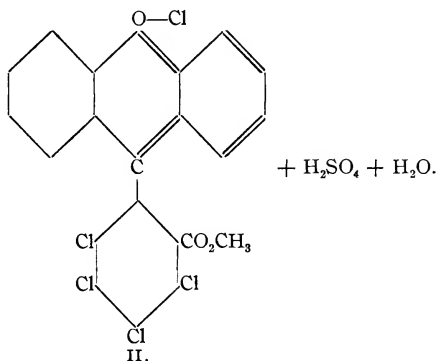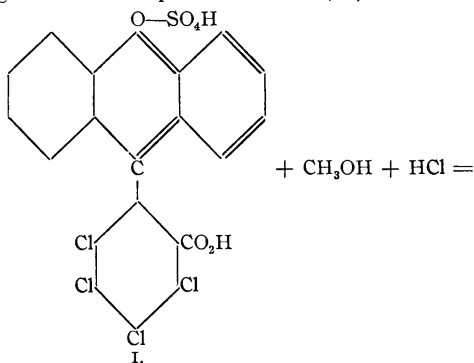
On distilling off the alcohol and treating with water only tetrachlorfluoran was obtained. An attempt to make the ethyl ester by treating a solution of the fluoran in alcoholic caustic potash with ethyl iodide also failed to give the product sought for. Five grams of the tetrachlorfluoran were dissolved in absolute alcohol and treated with one gram of caustic potash dissolved in absolute alcohol. An excess of ethyl iodide was then added and the mixture boiled for eight hours on a water bath in a flask connected with a reflux condenser. The alcohol was then evaporated off on the water bath and the residue treated with water to remove potassium iodide. The residue was crystallized several times from alcohol.

Analyses gave the following results:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.2562	15.70	21.72
II.	0.2048	12.55	21.72

$$\text{Calculated for } C_6H_4 {\overset{\displaystyle O}{\underset{\displaystyle C-OH}{\big\langle\quad\big\rangle}}} C_6H_4 \qquad , \qquad 29.30$$

$$C_6Cl_4CO_2C_2H_5$$
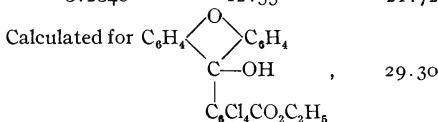
Chlorine has been removed and the product is not a derivative of tetrachlorfluoran. It dissolves in concentrated sulphuric acid with a yellow color but shows no fluorescence. Water reprecipitates the product unchanged.

Tetrachlorfluoran dissolves in concentrated sulphuric acid and in fuming nitric acid with a marked greenish yellow fluorescence and is precipitated unchanged from these solutions by water. It is possible that the color of these solutions is due to the formation of orthoquinoid oxonium nitrate or sulphate, having a structure analogous to Green and King's quinolphthalein hydrochloride:
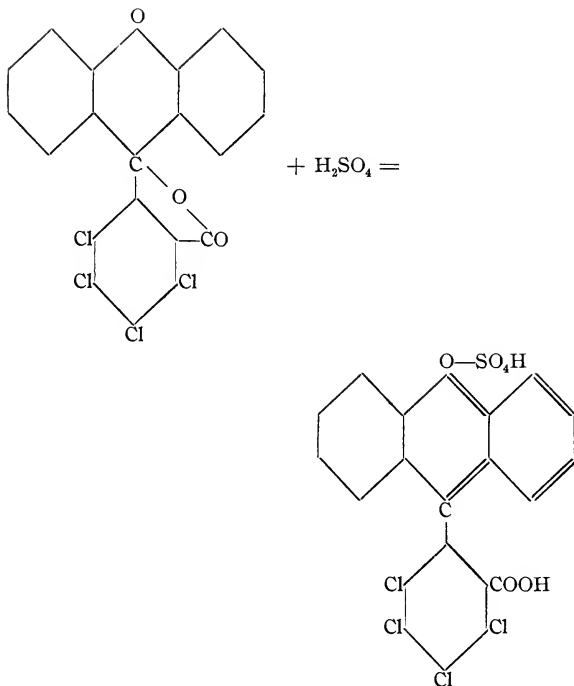
Attempts to prepare a colored hydrochloride of tetrachlor-fluoran were unsuccessful. The fluoran does not melt even when heated to 300°.

Phenoltetrachlorphthalein Diacetate.—Ten grams of pure phenoltetrachlorphthalein, ten grams of freshly fused sodium acetate, and fifty grams of Kahlbaum's pure acetic anhydride, were heated to boiling for one hour on a sand bath in a round-bottomed flask connected with a reflux condenser, the flask being shaken constantly to prevent charring of the materials. The warm liquid was then poured into one and a half liters

of water containing ice. The diacetate separated as an oil. After solidification the diacetate was filtered off on a Buchner funnel with the aid of suction and washed free from acetic acid and sodium acetate. The conversion of the phthalein into the diacetate was practically quantitative, a yield of 97 per cent of the calculated being obtained. The diacetate was recrystallized from benzene and obtained in a pure condition. Well-formed colorless crystals of the pure product were obtained by recrystallizing from absolute alcohol. These were examined by Professor Gill who reports as follows:

"The crystals are monoclinic, elongated in the direction of the ortho-axis, with an angle β of about 84°. Very variable measurements of the two end faces gave about 52° as their probable angle with the faces in the long zone. The double refraction is extremely high, and the extinction is parallel."

The air-dried product gave the following results on analysis:

	Weight of substance, gram.	Weight of silver chloride, gram.	Chlorine, per cent.
I.	0.1951	0.2070	26.23
II.	0.2027	0.2158	26.32
	Calculated for $C_{20}H_8Cl_4O_4(C_2H_3O)_2$,		26.27

The number of acetyl groups was then determined by a modification of the Wenzel method.[1] The diacetate was heated with 10 cc. of sulphuric acid (3:1), first on the water bath and then to boiling. After the addition of 25 cc. of the phosphate mixture the solution was distilled in steam, a Vigreux tube being used to prevent any mineral acid from being carried over mechanically. The 500 cc. of the distillate were titrated with tenth-normal potassium hydroxide solution, phenolphthalein being used as the indicator. This solution, acidified with hydrochloric acid, was then titrated with tenth-normal iodine solution to determine the sulphur dioxide present. This volume of the iodine solution was subtracted from that of the alkali, thus giving the corrected amount of the potassium hydroxide solution required to neutralize the acetic acid.

The analysis was made by Mr. H. W. Gillett.

[1] Monatsh. Chem., **18**, 659.

Weight of substance, gram.	N/10 iodine solution cc.	N/10 KOH solution (corrected), cc.	C_2H_3O, per cent.
0.296	0.10	10.9	15.84

Calculated for $C_{20}H_8Cl_4O_4(C_2H_3O)_2$,   15.94

Hence the product contains two acetyl groups.

The diacetate of phenoltetrachlorphthalein resembles the diacetate of phenolphthalein very closely in its properties. It is soluble in benzene, alcohol, and glacial acetic acid. It is saponified very slowly by cold aqueous alkalies or dilute sulphuric acid. Heating accelerates the saponification. Alcoholic solutions of the caustic alkalies saponify it readily, especially on heating, and the free tetrachlorphthalein may be obtained perfectly pure by neutralizing the solution with dilute acids and distilling off some of the alcohol. It is saponified at once by concentrated sulphuric acid.

The pure diacetate melted at 205°–206°.

As it is a colorless compound, it must have the structure

$$C_6Cl_4 \Big\langle {{C(C_6H_4OOCCH_3)_2} \atop {CO}} \Big\rangle O.$$
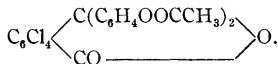
The Ethers of Phenoltetrachlorphthalein.

The Dimethyl Ether of Phenoltetrachlorphthalein.—Pure phenoltetrachlorphthalein (9.1 grams) was dissolved in pure absolute methyl alcohol and treated with about 1 gram of sodium dissolved in absolute methyl alcohol. An excess of methyl iodide was then added and the mixture was heated for one hundred and twenty hours in a round-bottomed flask connected with an upright condenser. A solution of 1 gram of sodium in methyl alcohol and methyl iodide was added from time to time as the red color of the solution disappeared. This excess of sodium methylate was added for the purpose of saponifying the colored ether ester and converting it into the sodium salt of the monomethyl ether, which was then transformed by the methyl iodide into the colorless dimethyl ether. When the addition of the sodium methylate no longer gave any color or only a faint pink color, the methyl alcohol and excess of methyl iodide were distilled off on the water bath and the residue remaining

in the flask was treated with water to remove the sodium iodide. The insoluble product was filtered off, washed with water, and dried. It contained the colorless dimethyl ether, a small quantity of the colored dimethyl ether ester, and some monomethyl ether. It was therefore boiled repeatedly with dilute sodium hydroxide solution for the purpose of removing any ether ester (by saponification), and monomethyl ether, together with any unchanged tetrachlorphthalein which might have been present. The residue was then filtered off, washed thoroughly with water, dried, and recrystallized twice from ethyl alcohol to obtain a perfectly pure, colorless product. Some of these crystals from alcohol were examined by Professor Gill who reports as follows:

"The crystals of the dimethyl ether of phenoltetrachlorphthalein are doubtless triclinic, usually in the shape of flattened needles or prisms. Optically they show an extinction angle of 0° to 6° with the long diameter, with the greater optical elasticity in this direction. The crystals are biaxial with a double refraction of 0.035 or more. On some crystals the two end faces were seen to make angles of 56° and 46°, respectively, with the direction of elongation."

The dimethyl ether is insoluble in aqueous solutions of the alkalies, but dissolves in a concentrated solution of alcoholic caustic potash without color, probably forming the potassium salt of the carbinol carboxylic acid,

$$C_6Cl_4\begin{cases} C(OH)(C_6H_4OCH_3)_2 \\ COOK \end{cases}.$$
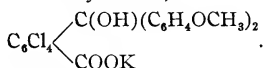
In concentrated sulphuric acid the dimethyl ether dissolves with a fine red color, purple in thin layers, and it is precipitated unchanged by water. The phenoltetrachlorphthalein gives a similar color but not so intense. The color is probably due to the formation of sulphates.

Analyses of the air-dried product gave the following results:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.1580	13.05	29.28
II.	0.1622	13.38	29.24
	Calculated for $C_{20}H_8Cl_4O_4(CH_3)_2$,		29.31

A determination of the number of methoxy-groups in this compound was made by Mr. H. W. Gillett by Decker's modification of Zeisel's method, the volumetric[1] being substituted for the usual gravimetric method. The following result was obtained:

Weight of substance, gram.	N/10 silver nitrate, cc.	CH_3O, per cent.
0.2268	9.5	12.99
	Calculated for $C_{20}H_8Cl_4O_4(CH_3)_2$,	12.82

Acetic anhydride was used with the hydriodic acid, as recommended by Herzig.[2]

The substance is therefore the dimethyl ether of phenoltetrachlorphthalein. The melting point of the pure product was found to be 152°–153°. As it is a colorless compound and is not saponified by alcoholic caustic potash it must be represented by the formula

$$C_6Cl_4 \diagdown \begin{matrix} C(C_6H_4OCH_3)_2 \\ CO \end{matrix} \diagup O.$$
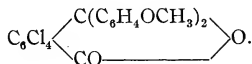
The Diethyl Ether of Phenoltetrachlorphthalein.—Attempts were made to prepare this ether by the method used in making the colorless dimethyl ether. After repeatedly extracting the product with sodium hydroxide solution it was washed with water, dried, and recrystallized a number of times from 75 per cent alcohol. The crystals were colorless and melted at 145°.

Analyses of the air-dried product gave the following results:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.1618	6.80	14.90
II.	0.1690	7.10	14.89
	Calculated for $C_{20}H_8Cl_4O_4(C_2H_5)_2$,		27.70

From the above results it is clear that chlorine has been removed and that the product is not a derivative of phenoltetrachlorphthalein. It was therefore not investigated further.

[1] Montash. Chem., **19,** 116 (1898).

[2] *Ibid.*, **9,** 544.

The case with which chlorine is removed from the phenol-tetrachlorphthalein is rather unexpected and surprising, especially since we had no difficulty in obtaining the colorless diethyl ether of tetrabromphenoltetrachlorphthalein by the same method.

The Monomethyl Ether of Phenoltetrachlorphthalein.—Phenol-tetrachlorphthalein (9.1 grams) dissolved in absolute methyl alcohol was treated with 0.92 gram of sodium in absolute methyl alcohol and heated for three hours with an excess of methyl iodide in a round-bottomed flask connected with an upright condenser. The alcohol and excess of methyl iodide were then distilled off on the water bath, the residue extracted, first with water and then repeatedly with sodium hydroxide solution. The monomethyl ether, together with any un-changed phenoltetrachlorphthalein which was present, were then precipitated from the alkaline filtrate with hydrochloric acid. More of the monomethyl ether was obtained by sapon-ifying a mixture of the colored ether ester and the colorless dimethyl ether with caustic potash in methyl alcohol, evaporat-ing to dryness on the water bath, and boiling the residue with water. The potassium salt of the monomethyl ether went into solution while the colorless dimethyl ether remained undissolved. After filtering the alkaline solution the mono-methyl ether was precipitated with hydrochloric acid, washed, and dried. To remove any phenoltetrachlorphthalein the product was treated several times with cold chloroform in which the tetrachlorphthalein is not very soluble. After filter-ing, the chloroform solution was evaporated to dryness on the water bath and the residue was crystallized from dilute acetone. Colorless crystals were obtained which, after drying in the air, gave the following results on analysis:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.2257	19.25	30.24
II.	0.1777	15.18	30.28
	Calculated for $C_{20}H_{19}Cl_4O_4CH_3$,		30.18

The monomethyl ether is extremely soluble in benzene and chloroform, which distinguishes it from the phthalein

itself. It is also easily soluble in acetone, methyl and ethyl alcohols, and in acetic acid. It dissolves in alkalies with a red color somewhat different from that of the alkaline solution of phenolphthalein. The lactone monomethyl ether of phenolphthalein, prepared by Meyer and Spengler,[1] also dissolves in alkalies, according to these authors, with a red color of less intensity than that produced by phenolphthalein itself. According to Green and King[2] this color is due to the presence of a small quantity of phenolphthalein in the monomethyl ether, since they found that the more completely they purified their monomethyl ether, the weaker was the color produced when it was dissolved in alkalies. They are of the opinion that the ether is directly converted by alkalies into the colorless carbinol salt:

$$\begin{array}{c} COO \\ | \\ C_6H_4 \end{array} C \begin{array}{c} C_6H_4OCH_3 \\ \\ C_6H_4OH \end{array} + NaOH = \begin{array}{c} CO_2Na \\ | \\ C_6H_4.C(OH) \end{array} \begin{array}{c} C_6H_4OCH_3 \\ \\ C_6H_4OH \end{array}.$$
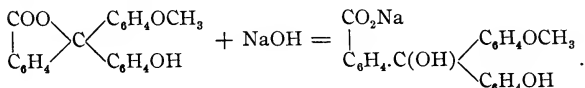
Further work will be necessary to determine whether this view is correct.

Nietzki and Burckhardt[3] found that the colorless monomethyl ether of tetrabromphenolphthalein also dissolves in dilute caustic alkalies without color.

In concentrated sulphuric acid the monomethyl ether of phenoltetrachlorphthalein dissolves with the same reddish yellow color as the phthalein itself and it is reprecipitated unchanged on the addition of water. It does not melt even when heated to 300°.

When boiled with acetic anhydride and sodium acetate it yields a colorless crystalline acetate. Professor Gill reports as follows in regard to the crystal from of the ether:

" The substance crystallizes form dilute acetone in colorless grains or scales with oblique extinction and medium high double refraction. The optical figure might be the obtuse bisectrix of a biaxial crystal or possibly normal to the axis of

[1] Ber. d. chem. Ges., **38**, 1318 (1905).

[2] J. Soc. Chem. Ind., **27**, 6 (1908).

[3] Ber. d. chem. Ges., **30**, 178 (1897).

a uniaxial crystal. The system is probably monoclinic or triclinic.''

As it is colorless, is not saponified by alcoholic caustic potash, and yields a colorless acetate, it must have the structure

$$
\begin{array}{c}
\text{COO} \\
| \qquad \\
\text{C}_6\text{Cl}_4
\end{array}
\Big\rangle
\text{C}
\Big\langle
\begin{array}{c}
\text{C}_6\text{H}_4\text{OCH}_3 \\
\\
\text{C}_6\text{H}_4\text{OH}
\end{array}
.
$$

Many attempts were made to prepare the *colored dimethyl ether ester,*

$$
\text{C}_6\text{Cl}_4
\Big\langle
\begin{array}{c}
\\
\text{C} \\
\\
\text{CO}_2\text{CH}_3
\end{array}
\Big\langle
\begin{array}{c}
\text{C}_5\text{H}_4\text{OCH}_3 \\
\\
\text{C}_6\text{H}_4 = \text{O}
\end{array}
,
$$
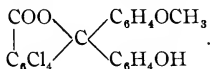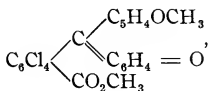
but it was found practically impossible to obtain it free from the colorless dimethyl ether. It is formed together with the monomethyl and dimethyl ethers, has a marked yellow color, is much more soluble in alcohol and benzene than the colorless dimethyl ether, and separates from these solvents in oily drops. It is saponified by heating with an alcoholic solution of caustic potash, yielding the potassium salt of the monomethyl ether.

Tetrabromphenoltetrachlorphthalein.—This substance was made according to the directions given by Baeyer for making tetrabromphenolphthalein. Ten grams of the phenoltetrachlorphthalein were placed in a round-bottomed flask connected with an upright condenser and dissolved in 125 cc. of boiling alcohol. Thirteen and six-tenths grams of bromine dissolved in the same amount of glacial acetic acid were then slowly added through the inner tube of the condenser to the boiling solution of the phthalein. The solution was then boiled for fifteen minutes to complete the reaction, the alcohol distilled off on the water bath, and the residue treated with water. The product was then filtered off on a Buchner funnel by the aid of suction and washed free from acid. The yield of the tetrabrom product was practically quantitative. Even after repeated crystallizations from alcohol the substance did not give satisfactory results on analysis. It was therefore converted into the diacetate by the method given under

phenoltetrachlorphthalein diacetate, and this was recrystallized from benzene. Analyses of this product having shown that it was pure, it was reconverted into the tetrabromphenol-tetrachlorphthalein by saponifying it in the cold with an alcoholic solution of caustic potash. When the saponification was complete the alkali was neutralized with hydrochloric acid, the alcohol distilled off, water added, and the product filtered off, washed with water, dried, and recrystallized from alcohol. The chlorine and bromine were determined in the air-dried material by the indirect method with lime with the following precautions: it was found that during the heating with lime either calcium chlorate or bromate was always formed, owing to the oxidizing action of the bromine. As silver bromate and chlorate are soluble the results for chlorine and bromine always come low. To overcome this difficulty one or two grams of sodium sulphite were dissolved in the water before the lime and nitric acid were added. On the addition of the nitric acid sulphur dioxide was set free and reduced any chlorate or bromate present to the chloride or bromide. This solution in dilute nitric acid was then filtered from carbonaceous and insoluble material from the lime, and the residue washed thoroughly with water. The chlorine and bromine in the filtrate were then precipitated with a measured excess of tenth-normal solution of silver nitrate as silver chloride and bromide. The precipitate was filtered off on a Gooch crucible, washed thoroughly, dried, and weighed. The excess of silver nitrate was then determined in the filtrate in the usual manner by titration with a standard solution of ammonium sulphocyanate, ammonium ferric sulphate being used as an indicator. Knowing the weight of the substance taken (A), the weight of the silver chloride and bromide (B), and the amount of the silver nitrate solution required to exactly precipitate the chlorine and bromine (C), the percentage of chlorine and bromine may be calculated by means of the following equations:

$$\text{Percentage of chlorine} = \frac{C - 53.224\,B}{0.66822\,A},$$

$$\text{Percentage of bromine} = \frac{69.745\,B - C}{0.38821\,A}.$$

Analyses of the air-dried tetrabromphenoltetrachlorphthalein gave the following results:

	A, weight of substance, gram.	*B*, weight of silver halides, gram.	*C*, N/10 AgNO₃, cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1900	0.3254	19.67	18.51	41.01
II.	0.2860	0.4898	29.60	18.47	41.09
	Calculated for $C_{20}H_6Cl_4Br_4O_4$,			18.38	41.44

It is interesting to note that nearly 60 per cent of this compound consists of chlorine and bromine and yet the substance has the properties of phenolphthalein. It does not melt even when heated to 300°. It is soluble in alcohol and benzene and crystallizes from hot benzene in colorless crystals. These were examined by Professor Gill, who reports as follows:

"The slightly brownish crystals occur in rather thick elongated plates, triclinic in form. They show an optical axis nearly normal to the large face. Dispersion is so strong that monochromatic light would be necessary to determine the extinction angle. Double refraction is strong, optical angle large, and optical character negative."

Tetrabromphenoltetrachlorphthalein is a stronger acid than phenoltetrachlorphthalein or phenolphthalein, but like both of these substances it is sensitive to carbonic acid and hence cannot be used as an indicator in place of methyl orange in titrating carbonates. It is recommended by E. Rupp and K. Seegers[1] for titrating strongly colored solutions of the quinine bases. It dissolves in solutions of sodium, potassium, ammonium, calcium, and barium hydroxides and in the alkaline carbonates with a blue color. The addition of large amounts of the alkalies to solutions in caustic soda or potash decolorizes the solution immediately, probably owing to the formation of the trisodium or tripotassium salt of the carbinol-carboxylic acid,

$$C_6Cl_4 \begin{cases} C(OH)(C_6H_2Br_2OK)_2 \\ COOK \end{cases}.$$
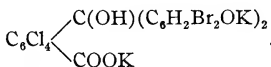
An aqueous solution of the disodium salt, when treated with a solution of copper sulphate, gives a deep blue precipitate of

[1] Apoth. Ztg., **22**, 748 (1907).

the copper salt of the phthalein. Lead acetate and silver nitrate solutions likewise give amorphous precipitates of the lead and silver salts, the lead salt having a lighter blue color than the silver salt. In cold concentrated sulphuric acid the phthalein is difficultly soluble with a yellowish red color. The addition of water discharges this color and precipitates the phthalein in an amorphous condition.

It does not form double salts with either aluminium chloride or stannic chloride.

An unsuccessful attempt was made to obtain a colored quinoid compound with the tetrabromphenoltetrachlorphthalein similar to the one from the tetraiodophenolphthalein described by Classen and Löb. Two grams of the tetrabromphenoltetrachlorphthalein were dissolved in a strong solution of sodium hydroxide and the solution cooled to 3°. On neutralizing carefully with hydrochloric acid, keeping the temperature at 3°, a colorless precipitate consisting of the tetrabromphenoltetrachlorphthalein was obtained. A colored hydrate is not formed under these conditions.

Tetrabromphenoltetrachlorphthalein does not form a methyl ester by the hydrochloric or sulphuric acid catalytic method. This is in accord with the Victor Meyer rule.

Assuming that in this compound the bromine atoms take the same positions as in the tetrabromphenolphthalein it must have the structure
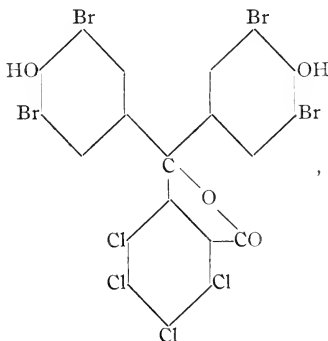
since it is a colorless compound and yields a colorless di-
acetate and a colorless dimethyl ether.

Tetrabromphenoltetrachlorphthalein   Diacetate.—The   same
method and same proportions of materials were used in the
preparation of this substance as in the case of the diacetate of the
phenoltetrachlorphthalein.   The yield was practically quantita-
tive.   The crude product was recrystallized from benzene and
obtained in a pure condition.   Crystals were also obtained
from absolute alcohol.

The following are the results of the analyses of the air-dried
product by the indirect method with lime:

	A, weight of substance, gram.	*B,* weight of silver halides, gram.	*C,* N/10 AgNO$_3$, cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1612	0.2461	14.84	16.17	37.14
II.	0.1880	0.2897	17.48	16.40	37.34
Calculated for C$_{20}$H$_4$Cl$_4$Br$_4$O$_4$(C$_2$H$_3$O)$_2$,				16.57	37.37

A determination of the number of acetyl groups present
was also made by a modification of the Wenzel method.[1]
The apparatus and chemicals were first tested with acetanilide
with the following result:

Weight of substance, gram.	N/10 sodium hydroxide, cc.	Acetyl, per cent.
0.4160	30.46	31.49
Calculated for C$_6$H$_5$NHCOCH$_3$,		31.84

With the diacetate the following result was obtained:

0.3880	9.45	10.47
Calculated for C$_{20}$H$_4$Cl$_4$Br$_4$O$_4$(C$_2$H$_3$O)$_2$,		10.05

Hence the substance must be a diacetate.   Professor Gill
has kindly furnished the following description of the crystals:

" The crystals are probably monoclinic, flattened parallel to
the plane of symmetry. β = about 88°.   The double re-
fraction is positive and very high.   The obtuse bisectrix is
normal to the surface of the flat plates.   Dispersion is so strong
as to interfere with accurate determinations of the extinction
angle, which is about 20° for average wave length of light."

The   diacetate   dissolves   in   concentrated   sulphuric   acid

[1] THIS JOURNAL, **26**, 121.

slowly with a yellowish red color exactly like that produced by the phthalein itself. It is also easily saponified by alcoholic caustic potash, less readily by boiling aqueous solutions of the alkalies. It is more readily soluble in alcohol, benzene, and glacial acetic acid than the phthalein itself.

The melting point of the pure product was found to be $190°-191°$.

As it is colorless and contains two acetyl groups it must have the structure
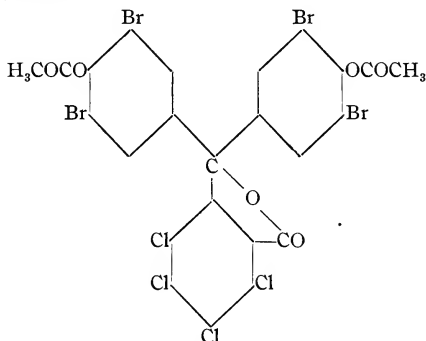
The Diammonium Salt of Tetrabromphenoltetrachlorphthalein. —A weighed amount of the pure phthalein was placed in a platinum boat and introduced into an apparatus through which was passed ammonia gas dried over soda-lime. The phthalein immediately became colored dark blue, owing to the formation of the ammonium salt. At the end of two hours the boat containing the ammonium salt was removed from the apparatus and allowed to remain exposed to the air for two minutes to permit any excess of ammonia to escape. The boat was then placed in a weighing tube, the stopper inserted, and the increase in weight ascertained. The following result was obtained:

Weight of substance, gram.	Weight of salt, gram.	Weight of NH_3 absorbed, gram.	Ammonia, per cent.
0.4080	0.4272	0.0194	4.54
	Calculated for $C_{20}H_4Cl_4Br_4O_4(NH_4)_2$,		4.23

The substance is therefore the diammonium salt. On allowing it to stand exposed to the air in a room free from acid fumes it gradually loses its deep blue color from the loss of ammonia, until it is finally white and returns to the original weight of the phthalein taken. Under these conditions, therefore, the phthalein yields a diammonium salt, which is unstable at ordinary temperatures in air free from ammonia. It is highly probable that this same salt is formed when the phthalein is dissolved in an excess of ammonia solution. When this solution is treated with excess of acid the phthalein is precipitated. Tetrabromphenoltetrachlorphthalein acts then as a dibasic acid, like tetrabromfluorescein or eosin, which forms a diammonium salt under the same conditions. It is very interesting to note that this transformation from the *colorless* phthalein to the *blue* diammonium salt and back again takes place here in the solid form as well as in solution. It is necessary therefore to assume that the change from the lactoid form to the quinoid and back again can also take place in *solids*. This change may be represented as follows:

$+ 2NH_3 =$
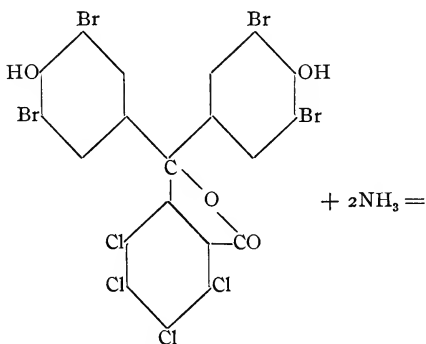
Tetrabromphenoltetrachlorphthalein
(lactoid form.)
Colorless.
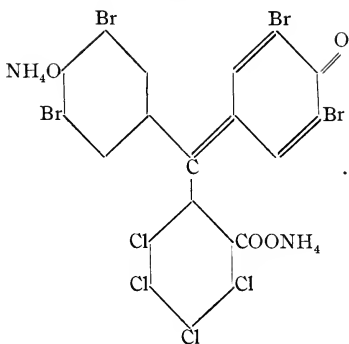
Diammonium salt
(quinoid form.)
Blue.

The Disilver Salt of Tetrabromphenoltetrachlorphthalein.—
The disodium salt was first prepared by dissolving 7.72 grams
of the phthalein in absolute alcohol and treating this solution
with 0.46 gram of sodium in absolute alcohol. The solution
was evaporated to dryness on the water bath and the blue
disodium salt resulting dissolved in water. The solution was
then filtered and a solution of silver nitrate added in excess.
The silver salt was precipitated as a light blue gelatinous mass.
This was filtered off on a Buchner funnel with suction, washed
free from silver nitrate, and dried, first on a porous plate and
then to constant weight in a vacuum desiccator over con-
centrated sulphuric acid. In the dried condition the silver
salt has a blue color. To analyze it, a weighed quantity was
placed in a Kjeldahl digestion flask and warmed on a sand
bath with *aqua regia.* In this way oxidation was effected and
all the silver bromide formed was converted into the chloride.
After the oxidation was completed, the *aqua regia* was evapo-
rated off and the silver chloride dissolved in ammonia to re-
move it from the flask and reprecipitated by adding nitric
acid. It was then filtered off on a Gooch crucible, washed,
dried, and weighed. The following are the results obtained:

	Weight of substance, gram.	Weight of silver chloride, gram.	Silver, per cent.
I.	0.5020	0.1450	21.74
II.	0.3134	0.0908	21.81
	Calculated for $C_{20}H_4Cl_4Br_4O_4Ag_2$,		21.90

The substance is therefore the disilver salt and is to be represented by the formula
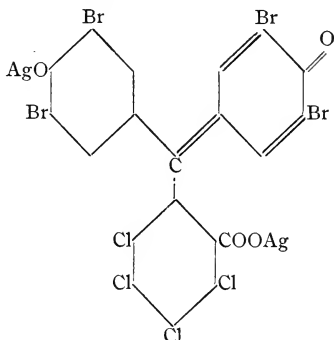
Ethers of Tetrabromphenoltetrachlorphthalein.

The Colorless Dimethyl Ether of Tetrabromphenoltetrachlorphthalein.—Tetrabromphenoltetrachlorphthalein (7.72 grams) was dissolved in absolute methyl alcohol in a flask connected with an upright condenser, and treated with a solution of 0.46 gram of sodium in absolute methyl alcohol. An excess of methyl iodide was then added and the contents of the flask were heated on the water bath to boiling. The colorless dimethyl ether which separated out after heating for a short time was filtered off from time to time as it accumulated. Sodium methylate in methyl alcohol and methyl iodide were added as the solution became decolorized, and the heating was continued for 72 hours. Seven and forty-five hundredths grams of the crude product, consisting almost entirely of the dimethyl ether, were obtained, a yield of 93 per cent of the calculated.

The product was crystallized from benzene after the monomethyl ether, the ether ester, and any unchanged phthalein

had been removed by boiling with caustic soda solution.

Analyses of the air-dried product by the indirect method with lime gave the following results:

	A, weight of substance, gram.	B, weight of silver halides, gram.	C, N/to silver nitrate, cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1862	0.3085	18.60	17.52	40.34
II.	0.1663	0.2750	16.60	17.66	39.96
	Calculated for $C_{20}H_4Cl_4Br_4O_4(CH_3)_2$,			17.73	39.99

The substance is therefore the dimethyl ether of tetrabromphenoltetrachlorphthalein. It is insoluble in dilute aqueous alkalies, but dissolves without color in alcoholic caustic potash on boiling, forming the potassium salt of the carbinolcarboxylic acid. The dimethyl ether is insoluble in cold concentrated sulphuric acid. It imparts not a trace of color to the acid and even when the mixture is heated to boiling the sulphuric acid takes on only a faint pink tint, which it loses on cooling. The basic properties of the phenolphthalein have been practically neutralized in this compound. The dimethyl ether is not very soluble in methyl or ethyl alcohols. It is soluble in ether, benzene, and glacial acetic acid. The pure product melts at 265°–266°. The crystals from benzene were examined by Professor Gill, who reports as follows:

"The crystals form cloudy needles with high double refraction and oblique extinction. They are surely monoclinic or triclinic, probably the latter."

As the dimethyl ether is colorless, insoluble in aqueous alkalies, and not saponified by alcoholic caustic potash, it must have the structure
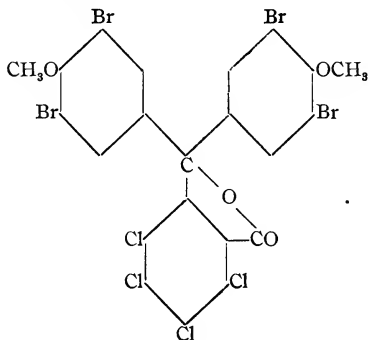
The Colorless Diethyl Ether of Tetrabromphenoltetrachlor-phthalein.—The same method was used in preparing this ether as in making the dimethyl ether The yield of the crude product, which consisted almost entirely of the diethyl ether, was 94 per cent of the calculated. As it is not very soluble in ethyl alcohol, it crystallized out as fast as formed, so that it was not acted on further by the sodium ethylate. This probably accounts for the fact that it was so easily obtained, while it was impossible to prepare a diethyl ether of phenol-tetrachlorphthalein by the same method, as the sodium ethylate removed chlorine from the compound.

The diethyl ether, after treatment with caustic soda solution to remove unchanged phthalein, monoethyl ether, and the ether ester (by saponification), was recrystallized from benzene. On analysis of the air-dried material by the indirect method with lime the following results were obtained:

	A, weight of substance, gram.	*B,* weight of silver halides, gram.	*C,* N/10 silver nitrate, cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1942	0.3112	18.80	17.26	38.52
II.	0.1812	0.2906	17.55	17.18	38.63
	Calculated for $C_{20}H_4Cl_4Br_4O_4(C_2H_5)_2$,			17.13	38.64

The product is therefore the diethyl ether of tetrabrom-phenoltetrachlorphthalein. It melts at 201°–202° when perfectly pure, and is colorless. The crystals from benzene were examined by Professor Gill, who reports as follows:

" The long white needles are seen under the microscope to be partly clear and translucent, but mostly cloudy as though they had undergone a paramorphic change. The clear crystals have parallel extinction and medium interference colors. The long diameter is the direction of greater elasticity. They are probably orthorhombic; optically positive, with small optical angle and plane of optical axes at right angles to the long direction."

The properties of the diethyl ether are similar to those of the dimethyl ether, and its structural formula is represented as follows:
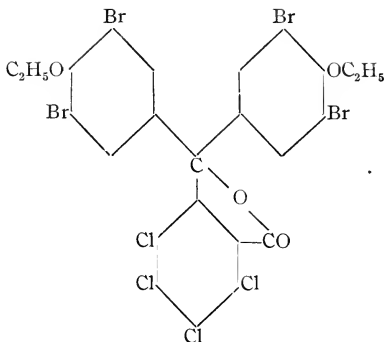
An attempt was made to prepare the colored, dimethyl
ether ester of the tetrabromphenoltetrachlorphthalein,

$$C_6Cl_4 \Big\langle \begin{array}{l} C \begin{array}{l} C_6H_2Br_2(OCH_3) \\ C_6H_2Br_2 = O \end{array} \\ COOCH_3 \end{array} \quad ,$$
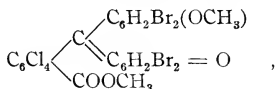
by the direct action of dry methyl iodide on the dry dipotassium
salt suspended in dry benzene, the method by which R. Meyer[1]
succeeded in preparing a colored, diethyl ether ester of phenol-
phthalein. After heating for 20 hours on the boiling water
bath no reaction had taken place. The dipotassium salt was
therefore converted into the disilver salt, which, when dry,
was suspended in dry benzene and heated with dry methyl
iodide, the method which R. Meyer used to prepare the colored
diethyl ether ester of tetrabromphenolphthalein (see page 353).
Reaction took place slowly and the benzene solution took on
a deep yellow color, showing the formation of the colored ether
ester. After 10 hours' heating the benzene solution was
filtered and evaporated to crystallization. Nothing but the
colorless dimethyl ether melting at 265° could be isolated,
however, and it is evident that, here, as in the case of the
colored ether esters of phenolphthalein and of tetrabrom-

[1] Ber. d. chem. Ges., **40**, 3603 (1907), and **41**, 2446 (1908).

phenolphthalein made by R. Meyer, the colored dimethyl ether ester of tetrabromphenoltetrachlorphthalein is first formed and is then converted into the colorless dimethyl ether.

SUMMARY.

The more important facts brought out in this paper may be summed up as follows:

1. Phenoltetrachlorphthalein and tetrabromphenoltetra-chlorphthalein, their diacetates, and dimethyl ethers have been prepared and analyzed. These are all colorless compounds and therefore probably have the lactoid structure,
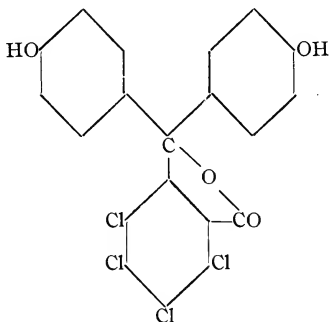
2. Phenoltetrachlorphthalein, like phenolphthalein itself, is a weak acid, its red, alkali salts being decomposed by the carbon dioxide of the air. The tetrabromphenoltetrachlor-phthalein is a stronger acid. We have prepared and analyzed its colored diammonium and disilver salts. The diammonium salt is unstable and gradually loses all of its ammonia on exposure to the air at ordinary temperatures. Both salts have a dark blue color and are therefore probably derived from the quinoid form of tetrabromphenoltetrachlorphthalein,
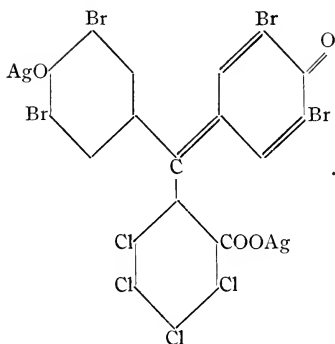
The transformation of the colorless lactoid form of tetra-bromphenoltetrachlorphthalein into the colored quinoid di-ammonium salt, and back again, therefore takes place in the *solid* form as well as in solution.

3. The acidifying influence of the four chlorine atoms in phenoltetrachlorphthalein or of the four chlorine atoms and four bromine atoms in tetrabromphenoltetrachlorphthalein is not sufficient to make these substances strong enough acids to be used as indicators for titrating carbonates. They can, however, be used as indicators in the same way as phenol-phthalein itself. Indeed, for titrating organic acids or alco-holic solutions, phenoltetrachlorphthalein is preferable to phenolphthalein.

4. Neither phenoltetrachlorphthalein nor tetrabromphenol-tetrachlorphthalein form esters by the catalytic method with hydrochloric acid or by the method with sulphuric acid. This is in accord with the Victor Meyer rule that two substituents in the ortho position to the carboxyl group retard or altogether inhibit the formation of esters.

5. Unlike phenolphthalein, phenoltetrachlorphthalein and tetrabromphenoltetrachlorphthalein do not combine with stannic or aluminium chlorides to form double salts, nor do they combine with hydrochloric acid.

Further work on tetraiodophenoltetrachlorphthalein, tetra-

nitrophenoltetrachlorphthalein, and tetrachlorfluorescein is in progress in this laboratory.

CORNELL UNIVERSITY,
February, 1909.

TETRACHLORPHTHALIC ACID.[1]

BY T. G. DELBRIDGE.

In collaboration with Dr. W. R. Orndorff, the author has been engaged for the past three years in an investigation of tetrachlorgallein and some of its derivatives. The results of this research are soon to be published in THIS JOURNAL. In order to obtain pure tetrachlorgallein, it was necessary to start with pure tetrachlorphthalic anhydride. The study of methods of purifying tetrachlorphthalic acid led to the discovery of certain inaccuracies in the literature concerning this substance and the following paper is presented for the purpose of correcting these errors and of making some additions to our knowledge of tetrachlorphthalic acid.

HISTORICAL.

Tetrachlorphthalic acid was first prepared in 1868 by Graebe,[2] by oxidation of pentachlornaphthalene in a sealed tube at 180°–200° with nitric acid (1.15–1.20). The product thus obtained was purified by sublimation and by crystallization from water. It was dried at 100° and analyzed with the following results: 0.2525 gram gave 0.8826 gram CO_2 and 0.0198 gram H_2O; 0.2778 gram gave 0.5281 gram AgCl.

	Calculated for $C_8H_2Cl_4O_4$.	Found.
C	31.58	31.77
H	0.66	0.87
Cl	46.71	47.02

It is to be noted that the weight of carbon dioxide is incorrectly given; it must have been 0.2942 gram (one-third of the weight given above), if the carbon found was 31.77 per cent.

[1] Read at the Baltimore meeting of the American Chemical Society.
[2] Ann. Chem. (Liebig), **149**, 18.

Graebe concludes from these analyses that the compound is tetrachlorphthalic acid and that it is a derivative of ortho-phthalic acid, since it resembles this compound in appearance and properties, especially in the formation of an anhydride. He states that the acid is easily soluble in hot water, slightly in cold. On rapid cooling of the hot saturated solution, color-less leaflets separate, while by slow crystallization, thick hard plates are obtained. The acid dissolves readily in alcohol and ether, melts at 250°, and changes, with loss of water, into the anhydride which melts at 245°. Analysis of the anhydride, prepared by sublimation, showed that it has the formula $C_8Cl_4O_3$, analogous to that of phthalic anhydride. In this paper Graebe describes very briefly the ammonium, lead, and silver salts of the acid, only the last being analyzed.

The preparation of tetrachlorphthalic acid in quantity by Graebe's method was of course impossible, since it involved the conversion of dichlornaphthoquinone into pentachlor-naphthalene by the action of phosphorus pentachloride. In 1882, however, tetrachlorphthalic acid was prepared com-mercially by a process kept secret at first but covered by patent in 1885. This process consisted in the direct chlorination of phthalic anhydride in the presence of antimony pentachlor-ide, the yield being almost quantitative. Thus it became possible for Graebe to make an extended study of the compound, and his second paper[1] on tetrachlorphthalic acid contains most of our knowledge of this compound up to the present time. According to this article, chlorination on the small scale by the factory method gave a mixture of tetrachlor-phthalic acid and acids containing less chlorine. The pure tetra-chlorphthalic acid was obtained from this mixture by crystal-lization from water. Chlorine, calculated for $C_6Cl_4(COOH)_2$, 46.71 per cent; found, 46.35 per cent. This acid proved to be identical in every respect with the one obtained by oxidation of pentachlornaphthalene and described in the first paper.[2] According to Graebe, the commercial acid is nearly pure, a direct chlorine determination giving 45.5 per cent, instead of

[1] Ann. Chem. (Liebig), **238**, 318.
[2] *Loc. cit.*

46.7 per cent, calculated. One crystallization of this product from water gave a perfectly pure acid, chlorine, 46.67 per cent. The properties of this acid agree with those reported in the first paper. The corrected melting point of the anhydride was found to be 252°, a short thermometer being used so that the mercury was entirely immersed in the bath. One hundred parts of water were found to dissolve 0.57 part of the acid at 14° and 3.02 parts at 99°. A large number of derivatives of the acid, including the potassium, barium, copper, and zinc salts, were prepared and studied by Graebe.

In 1886, the year before Graebe's second paper appeared, Claus and Wenzlik[1] oxidized β-heptachlornaphthalene with concentrated nitric acid (1.5) and obtained as one of the products tetrachlorphthalic acid. Purified by crystallization from water, it melted at 250° (uncor.) and gave on analysis:

	Calculated for $C_6Cl_4(COOH)_2$.	Found.
C	31.58	31.39
H	0.66	0.68
Cl	46.71	46.85

No additional information is given by these authors.

In 1892, Zincke and Günther[2] found that perchloracetophenone-*o*-carboxylic acid was decomposed by dilute alkalies, yielding chloroform and tetrachlorphthalic acid. The acid, purified by crystallization from hot water, agreed in all its properties with the tetrachlorphthalic acid described by Graebe. It crystallized in white, glistening leaflets which melted at 249°–250° with formation of bubbles. Allowed to harden and then heated again, the mass melted at 245°, which Graebe gives as the melting point of the anhydride. The acid was dried over sulphuric acid and analyzed:

	Calculated for $C_6Cl_4(COOH)_2$.	Found.
C	31.59	31.54
H	0.66	0.97
Cl	46.67	46.37

A number of other investigators have used tetrachlorphthalic acid in the preparation of other compounds, but as they

[1] *Ber. d. chem. Ges.*, **19,** 1166.

[2] *Ann. Chem.* (Liebig), **272,** 266.

give no analyses of the acid itself, their work need not be considered here. The following table presents a summary of that work on tetrachlorphthalic acid with which the author is especially concerned:

Date Observer	1868 Graebe.	1886 Claus, Wenzlik.	1887 Graebe.	1892 Zincke, Günther.	Calculated for $C_6Cl_4(COOH)_2$.
Acid dried	100°	?	?	H_2SO_4	. . . .
Carbon	31.77	31.39	. . . .	31.54	31.59
Hydrogen	0.87	0.68	. . . .	0.97	0.66
Chlorine	47.02	46.85	46.35 46.67	46.37	46.68
Melting point	250°	250°	250°	250°	. . . .
Crystal form	Leaflets Plates	. . . .	Leaflets Plates	Leaflets	. . . .
Melting point of anhydride	245°	. . . .	252° (cor.)	245°	. . . .

EXPERIMENTAL.

Determination of Chlorine.—A number of methods were tried at the beginning of the investigation. The sodium peroxide method of Pringsheim[1] was found to be unsatisfactory, as shown by the following analyses[2] of pure sublimed tetrachlorphthalic anhydride, dried at 180°:

Substance, gram.	Silver chloride, gram.	Chlorine, per cent.
0.5885	1.1715	49.26
0.5887	1.1638	48.92
0.5290	1.0491	49.07
0.5889	1.1783	49.51
0.4387	0.8861	49.98
	Calculated for $C_8Cl_4O_3$,	49.62

The next method tried was that described by Stepanow,[3] who decomposes the substance by the action of sodium on its alcoholic solution. In an analysis made by this method, 0.3347 gram of pure tetrachlorphthalic anhydride required 8.71 cc. of tenth-normal silver nitrate solution. Chlorine found, 9.23 per cent; calculated, 49.62 per cent. In a recent

[1] Ber. d. chem. Ges., **36**, 4244; **38**, 2429; This Journal, **31**, 386.
[2] International Atomic Weights for 1909 were used.
[3] Ber. d. chem. Ges., **39**, 4056.

article,[1] C. W. Bacon recommends a modification of the Stepanow method, stating that "If the simple directions are followed, success may be confidently expected in every case." This expectation is not realized in the case of tetrachlorphthalic anhydride, as shown by the following analysis: 0.1572 gram of pure tetrachlorphthalic anhydride was dissolved in 24.5 cc. of alcohol (98.1 per cent) and 3.1 grams of sodium added in small portions over a period of forty-five minutes. The mixture was then boiled for one hour and Bacon's directions followed in detail. 5.37 cc. of tenth-normal silver nitrate solution were required. Chlorine found, 12.11 per cent; calculated, 49.62 per cent. The extremely low results obtained by the Stepanow method and by Bacon's modification confirm the statement of Graebe[2] that tetrachlorphthalic acid dissolved in 96 per cent alcohol is for the most part unacted upon by sodium amalgam.

The method of determining chlorine finally adopted was a modification of the lime method, combined with titration according to Volhard. The combustion with lime is made in a Jena glass tube and the contents are transferred to an Erlenmeyer flask and dissolved in dilute nitric acid in the usual way. An excess of tenth-normal silver nitrate solution is then added slowly from a burette[3] and the flask closed with a rubber stopper and shaken vigorously for several minutes. The precipitate, consisting of carbon, silver chloride, and insoluble matter from the lime, is filtered off with suction on filter paper on a platinum cone and is washed thoroughly with dilute nitric acid. In the filtrate, which has a volume of 350–400 cc., the excess of silver nitrate is determined by titration with a tenth-normal solution of ammonium thiocyanate, ammonium ferric sulphate being used as indicator. The removal of silver chloride[4] and carbon by one filtration does not lessen the

[1] J. Am. Chem. Soc., **31**, 49.

[2] Ann. Chem. (Liebig), **238**, 323.

[3] The burettes used in this investigation were 25 cc. Schellbach burettes, 45 cm. long, graduated in 0.05 cc. and calibrated by the Herzogliches Sächsisches Eichamt, Gehlberg.

[4] The silver chloride must be removed before titration with ammonium thiocyanate. Compare Sutton: Volumetric Analysis (1904), page 144; Morse: Exercises in Quantitative Analysis (1905), page 220; Rosanoff and Hill: J. Am. Chem. Soc., **29**, 269 (1907).

accuracy of the results, the same values being obtained by gravimetric determination in the usual way and by the volumetric method, both with and without separate filtration of carbon and silver chloride. During the past three years, the author has made more than a hundred chlorine determinations by this method and the results have been uniformly satisfactory.

The tetrachlorphthalic acid used in the early part of the investigation was obtained from Kahlbaum. It was nearly white, melted at $253°-255°$ (cor.), and left no residue on ignition. On drying in a water oven at $98°$, the loss of weight was so large and so continuous as to prove that the anhydride is volatile at this temperature. Chlorine in the Kahlbaum acid, as received, was determined by the ordinary lime method:

Substance, gram.	Silver chloride, gram.	Chlorine, per cent.
0.2160	0.4156	47.61
0.3098	0.5954	47.56
Calculated for the acid, $C_6Cl_4(COOH)_2$,		46.68
Calculated for the anhydride, $C_8Cl_4O_3$,		49.62

In order to prove that this product is really a mixture of tetrachlorphthalic acid and its anhydride, twenty grams of the substance were extracted repeatedly with boiling water, in which the anhydride is practically insoluble. The residue, when dried, weighed five grams and dissolved completely in boiling sodium carbonate solution, carbon dioxide being set free. On acidifying this solution, tetrachlorphthalic acid was precipitated. Hence Kahlbaum's acid contains about twenty-five per cent of the anhydride.

This Kahlbaum acid was crystallized from water and the resulting product dried to constant weight at $20°$. On analysis for chlorine, 0.2163 gram of substance required 27.61 cc. of tenth-normal silver nitrate solution.

	Chlorine.
Found,	45.26
Calculated for $C_6Cl_4(COOH)_2$,	46.68
Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$,	45.34
Calculated for $C_6Cl_4(COOH)_2.H_2O$,	44.07

This analysis indicated either that the compound was impure or else that it contained a half-molecule of water. The purity of the acid was checked by determining its molecular weight by titration[1] with standard alkali and phenolphthalein. A weighed portion of the compound was suspended in 100 cc. of water in a Jena flask, about 0.5 cc. less than the required amount of tenth-normal sodium hydroxide solution added, and the slightly acid solution boiled for one minute to expel carbon dioxide. The titration was finished after cooling to 50° and adding the phenolphthalein. The sodium hydroxide was titrated under the same conditions against hydrochloric acid standardized by the silver chloride method.

In order to check the method and reagents, titrations were made on pure succinic acid, dried at 70°. The results were as follows:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.1244	20.96	118.7
0.1040	17.54	118.6
0.1200	20.32	118.1
0.1299	22.04	117.9
0.1346	22.73	118.4
0.1433	24.33	117.8
0.1423	24.11	118.0
Calculated for $C_2H_4(COOH)_2$,		118.05

The results obtained by titration of the crystallized tetrachlorphthalic acid are as follows:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3277	20.92	313.3
0.3250	20.71	313.9
0.3150	20.16	312.5
Calculated for $C_6Cl_4(COOH)_2$,		303.9
Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$,		312.9
Calculated for $C_6Cl_4(COOH)_2.H_2O$,		321.9

Hence the titration, like the chlorine determination, indicates that the acid really contains a half molecule of water,

[1] It was later found that Jacobson also recommends this method for determining water of crystallization. Ber. d. chem. Ges., **15**, 1854.

since the presence of any tri- or dichlorphthalic acid would lower the molecular weight.

An attempt was then made to drive off the half molecule of water by heating in an oven at 98°. The loss of weight was continuous, due to the volatility of the anhydride, amounting to 9.7 per cent in 118 hours, the calculated loss for the conversion of the acid, $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$, into the anhydride, $C_8Cl_4O_3$, being only 8.6 per cent. The product obtained in this experiment was insoluble in water and a chlorine determination showed that it was tetrachlorphthalic anhydride:

0.1640 gram of substance required 22.80 cc. of tenth-normal silver nitrate solution.

	Calculated for $C_8Cl_4O_3$.	Found.
Cl	49.62	49.30

The crystallized acid is therefore converted into the anhydride, even at 98°, and at this temperature the anhydride is somewhat volatile.

The acid used in the latter part of the investigation was procured from the Fabriques de Produits Chimiques de Thann et de Mulhouse, Alsace, through the Heller & Merz Company, Newark, New Jersey. This acid was nearly white, melted at 252°–254° (cor.), and contained less than two per cent of the anhydride. Titration of this acid with standard alkali by the method described gave for the molecular weight, 311.1 and 310.9; calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$, 312.9. Chlorine determinations on the acid, as received, gave the following results:

Substance, gram.	Tenth-normal silver nitrate, cc.	Chlorine, per cent.
0.1781	22.24	44.28
0.1793	22.43	44.36
Calculated for the acid with $\frac{1}{2}H_2O$,		45.34

Hence this acid is fairly pure. It is to be noted that Graebe[1] found 45.5 per cent of chlorine in the acid from this source.

This commercial tetrachlorphthalic acid was dissolved in acetone, in which it is excessively soluble, and the solution was

[1] Ann. Chem. (Liebig), **238**, 320.

decolorized with bone black, filtered, and poured into a large volume of water. Within a few minutes the acid began to crystallize in very thin leaflets which were filtered off, washed with cold water, and dried to constant weight at 20°. Chlorine determinations on this product gave the following results:

Substance, gram.	Tenth-normal silver nitrate, cc.	Chlorine, per cent.
0.1669	21.30	45.25
0.1701	21.70	45.24
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		45.34

The molecular weight of this acid was then determined by titration with tenth-normal sodium hydroxide solution. A decided improvement in the method already described[1] consists in the use of phenoltetrachlorphthalein[2] as the indicator. This compound has superseded phenolphthalein in the author's laboratory and is an indicator to be recommended very highly, possessing a real advantage over phenolphthalein in that it is somewhat less sensitive to carbon dioxide and that the end point is sharper. Using phenoltetrachlorphthalein as indicator, the following results were obtained on the crystallized tetrachlorphthalic acid:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3665	23.41	313.1
0.3702	23.64	313.2
0.3676	23.48	313.1
0.3742	23.89	313.3
0.3814	24.35	313.3
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9
Calculated for $C_6Cl_4(COOH)_2$,		303.9

The close agreement of these results with each other is due largely to the use of phenoltetrachlorphthalein as indicator. It is evident that titration is more accurate than chlorine determination in testing the purity of the acid.

Further proof that the crystallized tetrachlorphthalic acid contains a half molecule of water was furnished by the deter-

[1] Page 399.
[2] Orndorff and Black: THIS JOURNAL, **41**, 349.

mination of carbon and hydrogen. The Dennstedt[1] method of combustion was abandoned after two failures to secure complete oxidation. The combustion was eventually made by burning in oxygen with de Roode's[2] mixture of lead chromate and lead oxide, a silver roll being used in place of the copper gauze. The difficulty of oxidizing the compound is shown by the failure of the Dennstedt method and by the fact that in one instance tetrachlorphthalic anhydride sublimed through a 10 cm. layer of hot lead chromate mixture. Analyses:

I. 0.3535 gram of substance gave 0.3979 gram of carbon dioxide and 0.0379 gram of water.

II. 0.3453 gram of substance gave 0.3869 gram of carbon dioxide and 0.0348 gram of water.

	Found.		Calculated for $C_6Cl_4(COOH)_2$.	Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$.
	I.	II.		
C	30.69	30.55	31.59	30.68
H	1.19	1.12	0.66	0.97

The composition of the crystallized tetrachlorphthalic acid is therefore undoubtedly represented by the formula $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$, and not by the one found in the literature.

After several failures to dry the acid to constant weight in an oven heated to various temperatures, some of it was placed *in vacuo* with phosphorus pentoxide above and below.[3] The loss was slow and uniform but much greater than that required for the loss of a half molecule of water. Drying was discontinued after 302 days, the loss in that time amounting to 6.4 per cent, while that calculated for the loss of a half molecule of water is only 2.9 per cent. This loss, together with the fact that most of the dried substance was insoluble in boiling water, shows that tetrachlorphthalic anhydride is formed at room temperature under these conditions.

Although it was impossible to dry the crystallized acid to constant weight in an oven, it seemed likely that the rate of loss might give some indication as to the presence of the half

[1] Anleitung zur vereinfachten Elementaranalyse, Hamburg, 1906, S. 51.

[2] THIS JOURNAL, **12**, 226.

[3] This arrangement has been found extremely efficient in shortening the time required for drying.

molecule of water. The drying apparatus used for this pur-
pose was one devised in connection with the study of easily
oxidized derivatives of tetrachlorgallein. The idea is not a
new one[1] but the utility and simplicity of the apparatus justi-
fies a description of its essential features. The 500 cc. bal-
loon flask (A) of Jena glass contains 150 cc. of some liquid
of suitable boiling point. The vapors from the boiling liquid
pass through the jacket of the condenser (C), inclined at a
small angle, as shown, and are then returned to the flask,
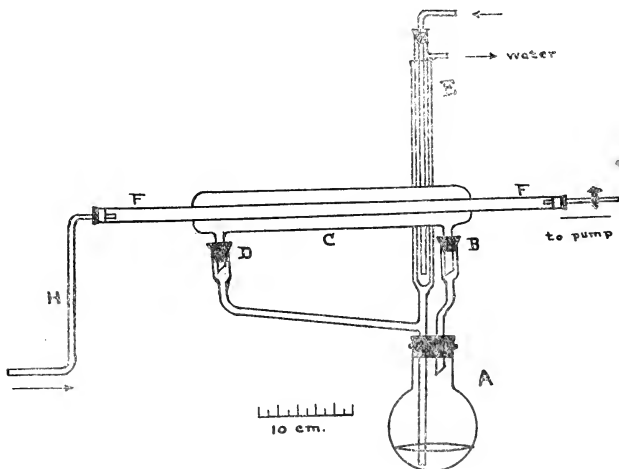
loss being prevented by the Beckmann condenser (E). The
condenser (C) is covered by a sheath of asbestos paper to pre-
vent radiation, so that the inner tube (F) is heated uniformly
to the temperature of the vapor surrounding it. The joints
(B) and (D) are made with corks, as shown. The apparatus
is supported on an iron stand by a clamp on the condenser
(C) and by an asbestos ring under the flask (A). Substances
are dried in boats which are pushed into the tube (F). One

[1] Compare Storch: Ber. d. österr. Ges. Förd. chem. Ind., **15**, 13.

end of this tube is closed by a rubber stopper carrying a glass tube drawn out to a capillary at (H) and connected through purification apparatus to a suitable gas supply. The other end of the tube (F) is connected with a suction pump by means of which the air may be removed from the apparatus, while hydrogen, carbon dioxide, or other suitable gas is allowed to enter through (H). By properly adjusting the size of the capillary (H), it is possible to maintain a constant flow of gas through the tube (F) at a pressure of only twenty millimeters. The constriction (H) is omitted in drying at atmospheric pressure. If even boiling of the liquid is ensured by the addition of broken porcelain, the temperature in the tube (F) is constant and uniform, even at 200° (nitrobenzene). The construction of this apparatus presents no difficulty, all of the parts needed being regular laboratory equipment. Among its advantages are the following: Very little gas is required for heating; drying is exceedingly rapid, especially when the entering gas is dried with phosphorus pentoxide; there is no danger of contaminating the substance; most important of all is the fact that the outflowing gas may be easily examined, qualitatively and quantitatively, for volatilized ammonia, hydrochloric acid, benzene, acetone, etc. Condensation of moisture on the cold part of the tube (F) furnishes a simple method for the detection of water of crystallization.

Pure crystallized tetrachlorphthalic acid was dried in this apparatus at 109° (toluene), weighings being made at half-hour intervals. The rate of loss decreased uniformly until the twelfth hour when the weight became practically constant (0.2 milligram lost in one hour). The cold part of the drying tube was partly covered with a very thin film of volatilized anhydride, so that the observed loss is a trifle higher than the calculated.

Substance, gram.	Loss, gram.	Water, per cent.
0.4136	0.0365	8.82
0.4291	0.0378	8.81
Calculated for loss of $1\frac{1}{2}H_2O$ from		
$C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$		8.64

The dried material was insoluble in boiling water and was further shown to be tetrachlorphthalic anhydride by its chlorine content. Found, 49.54 per cent; calculated, 49.62 per cent. Hence the crystallized acid is completely converted into tetrachlorphthalic anhydride at 109° with the loss of one and a half molecules of water, a further proof that the composition of the tetrachlorphthalic acid is represented by the formula $C_6Cl_4(COOH)_2.\tfrac{1}{2}H_2O$.

The crystallized acid corresponds in general to the description of Graebe.[1] It is slightly soluble in cold water, benzene, and chloroform, fairly soluble in hot water, alcohol and ether, while in acetone it is excessively soluble. Rapid cooling of the hot aqueous solution gave leaflets, slow crystallization by spontaneous evaporation at 20° gave thick plates. Slow cooling of the hot saturated solution in water gave fine needles, a form not mentioned by other investigators who have worked with this compound. The formation of these needlelike crystals is favored by the presence of a mineral acid.

Determination of the melting point of the acid gave results which do not agree with those obtained by previous investigators. All melting points given in this paper were taken with Anschütz[2] thermometers graduated in fifths of degrees and compared frequently with thermometers standardized by the Physikalisch-technisches Reichsanstalt. The thread of the mercury was entirely immersed in the sulphuric acid in every case and the observed melting point is therefore the corrected one. The apparatus used was that described by Thiele.[3] This simple device is a valuable addition to laboratory equipment and deserves general recognition. The only objection to its use lies in the fact that poorly annealed tubes crack when heated. For this reason the author uses a quartz tube obtained from Heraeus. The Thiele apparatus made of Jena glass is in general use in this laboratory and is very satisfactory. Using this apparatus, it was found that tetrachlorphthalic acid, heated in a capillary tube, began to melt at 255° and was not completely melted until 257°. Contrary to the

[1] *Loc. cit.*

[2] Destillation unter vermindertem Druck, Bonn, 1887, S. 16.

[3] Ber. d. chem. Ges., **40**, 996.

statement of Graebe, no loss of water was noted. When allowed to solidify and then heated again, the substance melted at the same temperature as before. Graebe[1] found that the acid melted at 250° (uncor.) with loss of water and formation of the anhydride which melted at 245° (uncor.) or 252° (cor.). Having already proven that tetrachlorphthalic acid is readily converted into the anhydride, even at 98°, the author suspected that the observed melting point was not that of the acid but of its anhydride. To verify this view, pure anhydride was prepared, first by drying the acid at 105°, secondly by sublimation of this product. The anhydride prepared in both these ways melted at 255°–257° (cor.) and melted at the same temperature when heated a second time. The melting point interval seems to be large for a pure compound but the same results were obtained with products repeatedly crystallized from different solvents. In order to determine more exactly the true melting point of the substance, it was heated for 35 minutes at 254°.2 in a sulphuric acid bath surrounded by the vapor of boiling diphenyl. No melting could be observed and the temperature was raised by adding a little diphenylamine to the boiling diphenyl. The compound was completely melted after five minutes' heating at 254°.8–255°.2 (cor.). The correct melting point of tetrachlorphthalic anhydride is therefore very close to 255°, and the melting point of the acid is not noted since it goes over into the anhydride at fairly low temperatures.

A number of attempts were next made to obtain the anhydrous acid. Pure crystallized tetrachlorphthalic acid was dissolved in boiling water and this solution allowed to cool very gradually. The acid crystallized in long, thin plates which were dried to constant weight at 20° and titrated with standard alkali:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3638	23.24	313.1
0.3620	23.13	313.0
0.3590	22.95	312.9
Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$,		312.9

[1] *Loc. cit.*

Determination of chlorine in this product confirms the above formula:

0.1769 gram of substance required 22.57 cc. of tenth-normal silver nitrate solution.

	Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$.	Found.
Cl	45.34	45.24

The melting point of this acid was $255°–257°$ (cor.) and its other properties were identical with those of the acid obtained by crystallization from very dilute acetone.

A solution of pure tetrachlorphthalic acid in water was allowed to stand for several weeks at $20°$. At the end of this time a considerable amount of thick, transparent plates had crystallized out. They were separated from the solution, dried to constant weight at $20°$, and titrated:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3612	23.06	313.3
0.3635	23.24	312.8
Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$,		312.9

These crystals melted at $255°–257°$ and had the other properties of the acid already described.

Pure tetrachlorphthalic acid was dissolved in water and the solution concentrated at the boiling point until a considerable amount of the acid had crystallized out. The solution was decanted at once, the crystals washed with a little hot water, and dried to constant weight at $20°$. Titration with alkali showed that this acid also contained the half molecule of water:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3647	23.30	313.0
0.3578	22.88	312.8
Calculated for $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$,		312.9

As was stated before, fine needles are obtained when the hot saturated solution in water is allowed to cool fairly rapidly. These needles melt at the same temperature as the acid crys-

tallized in other ways and give the same molecular weight on titration:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3842	24.57	312.7
0.3847	24.59	312.9
Calculated for $C_6Cl_4(COOH)_2 . \frac{1}{2}H_2O$,		312.9

Some of the pure acid was crystallized from anhydrous ether. The resulting crystals were extremely fine needles, melting at 255°–257° (cor.) and still containing the half molecule of water, as shown by the following determinations:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3812	24.34	313.1
0.3824	24.46	312.7
Calculated for $C_6Cl_4(COOH)_2 . \frac{1}{2}H_2O$,		312.9

Crystallized tetrachlorphthalic acid was boiled with 700 cc. of dry benzene, the benzene solution filtered from some undissolved acid, concentrated to 125 cc., and let stand overnight. The mass of slender prisms which separated was filtered off and allowed to dry. An attempt to titrate this product showed that it was insoluble in boilng water, a fact which indicated that it was the anhydride. Solution was finally effected by boiling for two to three hours with a large excess of standard alkali. The solution was then made slightly acid with tenth-normal hydrochloric acid, boiled to remove carbon dioxide, and titrated with sodium hydroxide, phenol-tetrachlorphthalein being used as indicator:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3743	26.18	286
0.4626	32.22	287
Calculated for $C_8Cl_4O_3$,		286

Further proof that the compound crystallized from benzene is really tetrachlorphthalic anhydride is furnished by its chlorine content. Chlorine calculated for $C_8Cl_4O_3$, 49.62 per cent; found, 49.53 and 49.45 per cent.

An attempt to crystallize the acid from benzene without distilling off any of the solvent, gave a product which also contained some anhydride detected by its insolubility both in boiling water and dilute alkali. Crystallization from dry chloroform likewise gave a mixture of the acid and its anhydride, as shown by determination of its molecular weight by the method used in titrating the anhydride obtained by crystallization from benzene. 0.3141 gram of substance required 21.32 cc. of tenth-normal sodium hydroxide. Molecular weight, 295. These experiments give still further proof of the great ease with which tetrachlorphthalic acid is converted into tetrachlorphthalic anhydride.

Pure tetrachlorphthalic acid was crystallized from absolute methyl alcohol. The air-dried product melted at 254°–256° and contained some monomethyl ester, as shown by titration:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Combining equivalent.
0.3665	22.27	164.6
0.3757	22.43	167.5
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		156.4
Calculated for $C_6Cl_4\!\!\begin{array}{l}\diagup COOH\\ \diagdown COOCH_3\end{array}$,		317.9

A second crystallization from methyl alcohol gave a mixture containing still more of the monomethyl ester. This product melted at 135°–140°, became solid again on further heating, and then melted at 255°–257°. V. Meyer and Sudborough[1] state that the melting point of pure monomethyl ester of tetrachlorphthalic acid is 142°, the substance becoming solid on further heating, and yielding tetrachlorphthalic anhydride which melts at 250°, according to these authors. The presence of methyl ester was further proved by titration: 0.3084 gram of substance required 11.40 cc. of tenth-normal sodium hydroxide; combining equivalent, found 270.5; calculated for the acid, 156.4; for its monomethyl ester, 315.9. Crystallization from alcohols was therefore abandoned.

[1] Ber. d. chem. Ges., **27**, 3149.

Solutions of tetrachlorphthalic acid in dry acetone gave, on standing, large transparent crystals which lost acetone on exposure to air, soon crumbling to a white powder. This powder was allowed to stand until it had no odor of acetone, being stirred from time to time. Titration then showed that the compound contained the half molecule of water. More crystals from acetone were prepared, dried rapidly with filter paper, and weighed at once in a stoppered bottle. A slow current of air, dried with calcium chloride, was passed through the bottle until the weight became constant. The loss was 29.3 per cent; calculated for two molecules of acetone, 27.6 per cent.[1] The resulting product was white, melted at 255°–257°, and possessed the other properties of the acid with a half molecule of water. Titration, however, showed that this compound was the long-sought *anhydrous* acid:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3662	24.10	303.9
0.3656	24.04	304.2
0.3693	24.31	303.8
0.3722	24.49	304.0
Calculated for $C_6Cl_4(COOH)_2$,		303.9

In order to prove that this compound was really the anhydrous acid, some of it was converted into tetrachlorphthalic anhydride by drying at 109° in the apparatus already described. The same thin film of volatilized anhydride was formed on the cold part of the tube, as was observed in drying the acid containing a half molecule of water.[2]

0.8220 gram of substance lost 0.0500 gram.

	Calculated for conversion of $C_6Cl_4(COOH)_2$ into $C_8Cl_4O_8$.	Found.
Water	5.93	6.08

The anhydrous acid is unstable, taking up water from the air with the formation of the acid containing a half molecule of water, which was also obtained directly by leaving the

[1] The simultaneous loss of two molecules of acetone and a half molecule of water would amount to 29.2 per cent.

[2] Page 404.

acetone compound in the air of the laboratory. This fact, together with repeated failure to obtain the anhydrous acid by crystallization, leads the author to conclude that the *anhydrous* tetrachlorphthalic acid has never been prepared before. The results of the analyses given in the literature[1] can be easily explained on the assumption that previous investigators dried the acid and hence analyzed a mixture of tetrachlorphthalic anhydride and tetrachlorphthalic acid containing the half molecule of water.

It follows, therefore, from the experimental data presented that tetrachlorphthalic acid obtained by crystallization has the composition represented by the formula $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, or better, $(C_8H_2O_4Cl_4)_2 \cdot H_2O$. The structural formula of the acid is probably
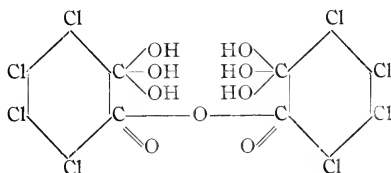
or possibly
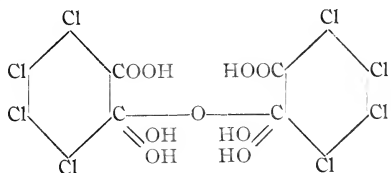
Proof of either formula is not available at present.

An attempt was made to determine the molecular weight of the compound by the boiling point method. The solubility in chloroform, benzene, and water is too low. Determinations were made with ether and also with acetone before it was learned that the acid forms a compound with acetone.

Although no weight can be given to these results with our

[1] Tabulated on page 396.

present knowledge of the state of solution, the data obtained are given below:

Solvent.	Substance, gram.	Solvent, grams.	Rise.	Constant.	Molecular weight.
Ether	0.733	23.3	0°.205	21.1	324
Ether	0.691	28.8	0°.150	21.1	337
Acetone	0.967	31.5	0°.235	17.1	223
Acetone	0.691	26.8	0°.210	17.1	210
Water	0.850	45.3	0°.033	5.2	296

In order to test the correctness of the accepted formula for *phthalic* acid, the author made titrations on this compound, using phenoltetrachlorphthalein as indicator:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.1965	23.69	165.9
0.1925	23.17	166.2
0.1948	23.47	166.0
Calculated for $C_6H_4(COOH)_2$,		166.05

These results not only prove the correctness of the usual formula for phthalic acid, but also indicate the accuracy of this method of analysis.

Crystals of tetrachlorphthalic acid obtained in various ways were examined by Professor A. C. Gill, of the Mineralogical Department of the University, and he makes the following report:

"As is the case with phthalic acid, slight differences in the conditions of crystallization of this substance produce marked variations in the habitus of the resultant crystals. Though these reach a diameter of about two mm., it has not as yet been possible to obtain accurate measurements of them. There is little doubt, however, that the substance is monoclinic. It very likely belongs to the dogmatic class, since it was frequently observed that the two prismatic faces on either side of the plane of symmetry were much striated, while their parallels gave fairly clear reflection images.

"The commonest shape is that of thin hexagonal or rhombic tablets. The rhombic plates show a plane angle of 47°, and those of hexagonal shape have this angle truncated by faces of the ortho-zone which may either be very small, or, in some

cases, much larger than the prismatic faces which produce the rhombic shape. These crystals are optically biaxial, positive, with strong double refraction, and the clinopinacoid as the optical axial plane. An obtuse bisectrix stands nearly normal to the tabular face. Extinction is parallel to the trace of the ortho-zone faces.

"Slow growth in water solution produced stout crystals of rhombohedral appearance bounded by four prismatic faces and a basal pinacoid. On some of these an ortho-dome was so largely developed as to produce an *octahedral* habitus."

The purification of very impure tetrachlorphthalic acid was next studied. A mixture was prepared containing 75 per cent tetrachlorphthalic acid, melting at 252°–254°, and 25 per cent commercial dichlorphthalic acid, which melted at 105°–135°. The melting point of the mixture was 220°–240°. Purification was carried out as follows:

A. Fifty grams of this mixture were crystallized from 1500 cc. of water, bone black being used to decolorize the solution. The product, which was yellow, weighed 22 grams when dried at 20°, and melted at 251°–254° (cor.).

B. The substance obtained in *A* was recrystallized from 800 cc. of water. The yellow product dried at 20° weighed 17 grams and melted at 254°–256° (cor).

C. Fifty grams of the original mixture were dissolved in 150 cc. of acetone, the solution filtered, poured into 1200 cc. of water, and let stand for three hours. The crystals which separated were filtered off and dried at 20°. Yield: 23 grams of a white product melting at 251°–255° (cor.).

D. Fifty grams of the original mixture were boiled with 350 cc. of water containing 15 grams of sodium hydroxide and the solution filtered and again heated to boiling. An excess of hydrochloric acid, 1.10, was added very slowly, the solution being kept boiling vigorously by passing steam into it. Boiling in this way was continued for ten minutes and the solution filtered from the precipitated acid while hot. This acid was washed once with boiling water, then with cold water until free from chloride, and dried at 20°. This product was perfectly white, weighed 31 grams, and melted at 249°–

254°. The hot filtrates gave a crop of yellow crystals weighing 5.5 grams when dry.

The purity of these products was determined by the titration method described and the results, together with the melting points and percentage yield, are given in the following table:

	Substance, gram.	Tenth-normal sodium hydroxide, cc.	Mol. wt.	M. P.	Yield, per cent.
A.	0.3653	23.43	311.8	251°–254°	59.
	0.3650	23.43	311.6	....	...
B.	0.3825	24.46	312.8	254°–256°	45.
	0.3815	24.38	313.0	....	...
C.	0.3831	24.55	312.1	251°–255°	61.
	0.3589	23.00	312.1	....	...
D.	0.3773	24.35	309.9	249°–254°	83.
	0.3813	24.62	309.8	....	...
	Pure acid,		312.9	255°–257°	...

The purification of tetrachlorphthalic acid is therefore easily accomplished, the melting point is a reliable criterion of purity, and titration affords an easy way of checking the purity of the acid.

The following method of purifying the commercial acid gives perfect satisfaction: Boil 300 grams of this acid with two liters of water containing 45 grams of sodium hydroxide and filter the hot solution with suction on an 18 cm. Buchner funnel with a hardened filter. Heat the filtrate to boiling in a five-liter balloon flask by passing steam into it. Add gradually in the course of five minutes, 200 cc. of hydrochloric acid, 1.10, keeping the mixture boiling vigorously. Continue the boiling for thirty minutes longer and filter at once through an 18 cm. Buchner funnel with hardened filter, using strong suction. Transfer the precipitate to the balloon flask with 200 cc. of water, add 10 cc. of concentrated hydrochloric acid, and boil with steam for ten minutes. Filter at once as before, wash the precipitate with very cold water until it is free from chloride, and dry to constant weight at 20°. The product, which should be perfectly white, is pure tetrachlorphthalic acid, $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$. The yield is 240–260 grams,

about 80 per cent of the commercial acid used. The hot filtrates yield, on cooling, about 30 grams of a fairly pure acid which may be further purified as described, giving a total yield of about 90 per cent.

Tetrachlorphthalic Anhydride.

Tetrachlorphthalic acid may be converted into tetrachlorphthalic anhydride in a number of ways, as shown in the preceding pages. The anhydride has the composition represented by the formula $C_8Cl_4O_3$, as given by Graebe.[1] The substance used in analysis I., below, was obtained by drying tetrachlorphthalic acid, $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$, at 109°. Analysis II. was made on sublimed anhydride. Tetrachlorphthalic anhydride, obtained by crystallizing the acid from dry benzene, as already described,[2] was analyzed by Mr. C. K. Ou and his results are given in III. and IV.

	Substance, gram.	Tenth-normal silver nitrate, cc.	Chlorine, per cent.
I.	0.1618	22.61	49.55
II.	0.1610	22.49	49.53
III.	0.2130	29.75	49.53
IV.	0.2651	36.97	49.45
Calculated for $C_8Cl_4O_3$,			49.62

The melting point of pure tetrachlorphthalic anhydride is 255°–257° (cor.) and not 252° (cor.), as given by Graebe. It is practically insoluble in boiling water and is disssolved very slowly by boiling tenth-normal sodium hydroxide.

The sublimed tetrachlorphthalic anhydride was submitted to Dr. Gill, who makes the following report:

"The somewhat flattened colorless needles reach a length of five or six mm., but are not more than 0.3 mm. in maximum transverse diameter. No measurements of end faces could be obtained. The following data, however, indicate beyond reasonable doubt that the substance occurs in monoclinic crystals, elongated in the direction of the ortho-axis. The three pairs of faces which are most prominent in the zone

[1] Ann. Chem. (Liebig), **149**, 20.
[2] Page 408.

of elongation gave on the reflecting goniometer the following mean angles of mutual inclination: 46°52′, 41°53′, and 91°15′. Extinction is parallel in all positions of the needles when mounted in wax and rotated around their long axes between crossed Nicol prisms. Double refraction is strong. The plane of the optical axes is the clinopinacoid, *i. e.*, across the needles, and the bisectrix of a large optical angle (probably obtuse) emerges somewhat inclined from normal to the plane of flattening. If this angle, which was not measured, is obtuse, the substance is optically negative."

SUMMARY.

The more important facts brought out in this paper may be found in the following summary:

1. Tetrachlorphthalic acid crystallized from water under various conditions has the composition represented by the formula $C_6Cl_4(COOH)_2.\frac{1}{2}H_2O$, as shown (*a*) by determination of carbon, hydrogen, and chlorine; (*b*) by determination of the molecular weight of the acid by titration with sodium hydroxide; (*c*) by the weight lost in the conversion of the acid into its anhydride.

2. Tetrachlorphthalic acid with the half molecule of water may be crystallized from anhydrous ether without change.

3. Tetrachlorphthalic acid is very easily converted into its anhydride, $C_8Cl_4O_3$, this conversion having been brought about (*a*) by sublimation; (*b*) by drying at 98°; (*c*) by crystallization from a benzene solution concentrated by distillation; (*d*) by drying for a long time *in vacuo* with phosphorus pentoxide.

4. The correct melting point of tetrachlorphthalic anhydride is 255°–257°. The acid, when heated in a melting point tube, is converted into the anhydride and hence the melting point observed is the same as that of the anhydride.

5. Crystallization of tetrachlorphthalic acid from acetone gave a compound containing two molecules of acetone. When this compound is placed in a current of dry air at room temperature, it loses all its acetone and forms the *anhydrous*

tetrachlorphthalic acid, $C_6Cl_4(COOH)_2$. This anhydrous acid takes up moisture from the air, giving the stable acid

$$C_6Cl_4(COOH)_2 . \tfrac{1}{2} H_2O.$$

6. A simple apparatus is described for drying substances in a current of an indifferent gas at temperatures up to 200° and at low pressure if desired. This apparatus also permits the collection and examination of substances volatilized during drying.

In conclusion, the author desires to acknowledge his indebtedness to Professor A. C. Gill for the description of crystals and especially to Professor W. R. Orndorff for valuable advice throughout the investigation. The study of tetrachlorphthalic acid is being continued and another paper will appear at an early date.

CORNELL UNIVERSITY.
March 6, 1909.

THE ACTION OF ALKALINE HYDROXIDES ON α-BROMKETONES.

BY E. P. KOHLER.

In the course of some work on unsaturated ketones, I had occasion to study the reaction between potassium hydroxide and certain α-bromketones that, for the most part, may be regarded as derivatives of α-brompropiophenone. I found that the result of the reaction depends to an unusual degree upon the number, character, and location of the hydrocarbon residues contained in the ketone. The two typical reactions are represented by the equations:

I. $(C_6H_5)_2CHCBr(C_6H_5)COC_6H_5 + KOH =$
$(C_6H_5)_2C:C(C_6H_5)COC_6H_5 + KBr + H_2O$
II. $(C_6H_5)_2CHCBr(CH_3)COC_6H_5 + KOH =$
$(C_6H_5)_2CHCOH(CH_3)COC_6H_5 + KBr.$
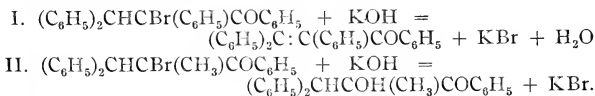
The unsaturated ketones formed according to the first equation are not affected by potassium hydroxide, but α-oxyketones are exceedingly sensitive to alkaline reagents, hence the occurrence of the second reaction was, in some cases,

inferred from the nature of the secondary products that were obtained.

The behavior of a number of α-bromketones is shown in the following table, which gives only the percentage of unsaturated ketone, the remainder of the product being composed either of oxyketones or of substances formed from these by secondary reactions:

	Per cent.
$(C_6H_5)_2CHCBr(C_6H_5)COC_6H_5$[1]	100
$(C_6H_5)(C_2H_5)CHCBr(C_6H_5)COC_6H_5$[2]	1-2
$(C_6H_5)_2CHCHBrCOC_6H_5$[3]	35-40
$(C_6H_5)_2CHCHBrCOC_6H_4OCH_3$[4]	35-40
$(C_6H_5)_2CHCHBrCOC(CH_3)_3$[5]	95
$(C_6H_5)_2CHC(CH_3)BrCOC_6H_5$[6]	none
$(C_6H_5)(C_2H_5)CHCHBrCOC_6H_5$[7]	none

From the behavior of these substances I concluded that this reaction does not give an unsaturated ketone unless the bromketone contains 2 aryl groups in the β position.

At a meeting of the *Gesellschaft deutscher Naturforscher und Aerzte*, held in 1906, Klages announced that he had obtained phenylvinyl ketone by treating brompropionylbenzene with potassium hydroxide. The report of the meeting does not state whether the α- or β-brom substitution product was used, but in a paper read before the Chemical Society at Heidelberg in 1908, Klages[8] stated that phenylvinyl ketone and its homologues are easily obtained by the action of potassium hydroxide on α-brom derivatives of the corresponding saturated ketones. The products are described as intensely yellow, mobile liquids that boil without decomposition.

Klages presented no evidence that these yellow liquids are really unsaturated ketones. The only reaction discussed by him is that with organic magnesium compounds. He found that, "contrary to expectation," the substances reacted with two molecules of alkylmagnesium halides, one combining with the carbonyl, the other with the ethylene group. The resulting magnesium derivative, when decomposed with water,

[1] THIS JOURNAL, **38**, 559.
[2] *Ibid.*, **35**, 399.
[3] *Ibid.*, **31**, 652.
[4] *Ibid.*, **38**, 541.
[5] *Ibid.*, **38**, 549.
[6] *Ibid.*, **38**, 552.
[7] *Ibid.*, **36**, 537.
[8] Report by Klages: Chem. Ztg., **1908**, p. 318.

gave a saturated tertiary alcohol with an alkyl group in the α position. The reaction between phenylvinyl ketone and methylmagnesium iodide, for example, is represented by the equation:

$$C_6H_5COCH:CH_2 + 2(CH_3 + H) =$$
$$C_6H_5COH(CH_3)CH(CH_3)CH_3.$$
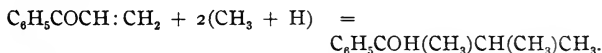
With phenylmagnesium bromide Klages obtained a reaction that he considers "normal"—addition of one molecule of the magnesium compound to form a derivative of an unsaturated alcohol. Thus with phenylpropenyl ketone:

$$C_6H_5COCH:CHCH_3 + (C_6H_5 + H) =$$
$$(C_6H_5)_2COHCH:CHCH_3.$$
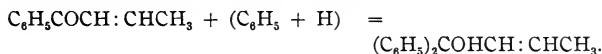
As evidence in favor of this interpretation Klages states that the product loses water when heated with oxalic acid, and passes into a hydrocarbon boiling at 297°—"one of the few allene derivatives of which the constitution is known with certainty."

These results are at variance with those obtained with all other unsaturated ketones. If correct, they would mean that the physical and chemical properties of these unsaturated ketones are entirely different from those of substances so closely related to them as crotonic aldehyde,[1] acetalacetone,[2] chloralacetophenone,[3] mesityl oxide,[4] and benzalacetophenone.[5] They would mean, also, that organic magnesium compounds are capable of combining directly with the ethylene group, a process that it has not been possible to carry out with any other class of unsaturated compounds. For these reasons I thought it desirable to repeat the experiments of Klages. I have found, as expected, that he had no unsaturated ketones.

The reaction between potassium hydroxide and α-brompropionylbenzene gave a mixture from which it was comparatively easy to separate a fraction boiling fairly constantly

[1] *Ber. d. chem. Ges.*, **41**, 3200.
[2] THIS JOURNAL, **38**, 526.
[3] *Ibid.*, **38**, 548.
[4] *Ibid.*, **38**, 528.
[5] *Ibid.*, **38**, 548.

between 217° and 219°—which Klages gives as the boiling point of phenylvinyl ketone. The composition of the yellow liquid, however, did not agree with that calculated for this substance. As different preparations invariably gave different analytical results, it was evident that the liquid contained substances extremely difficult, if not impossible, to separate by distillation. I therefore tried the reaction with the parabrom derivative of α-brompropionylbenzene in the hope of getting solid products. This ketone likewise gave a yellow liquid that boiled almost at a constant temperature under diminished pressure, but by repeated fractional distillations it was possible to separate a fraction that partially solidified in a freezing mixture. The bright yellow solid was found to be p-bromphenylmethyl diketone, $BrC_6H_4COCOCH_3$.

As this is a methyl ketone it was easy to remove it completely by digesting the mixture with acid sulphite. By further distillation, the residue was finally separated into p-brompropiophenone and p-brombenzoylmethylcarbinol:

$$BrC_6H_4COCH_2CH_3 \quad \text{and} \quad BrC_6H_4COCHOHCH_3.$$
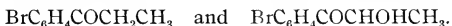
By a similar procedure it was possible to prove that the liquid that Klages regarded as phenylvinyl ketone was, in reality, a mixture of methylphenyl diketone boiling at 217°–219°, propiophenone boiling at 220°–221°, and benzoylmethylcarbinol which distils with the others but decomposes when heated by itself.

No unsaturated ketones could be detected among the products of the reactions described and none was obtained by the action of potassium hydroxide on α-bromisobutyl-p-bromphenyl ketone,

$$(CH_3)_2CHCHBrCOC_6H_4Br.$$

As this ketone has a tertiary hydrogen atom in the β position, it would be expected to lose hydrobromic acid as readily as any ketone of this type, but it gives only products analogous to those obtained with α-brompropionylbenzene. It may be asserted with considerable confidence, therefore, that unsaturated ketones of the type of benzoylethylene cannot be made by the action of alkaline hydroxides on α-bromke-

tones. The substances that Klages obtained by treating his
yellow liquids with organic magnesium compounds are not
derived from unsaturated ketones and his interpretation of
this reaction is erroneous.

The diketones obtained by the action of potassium hy-
droxide on α-bromketones are formed in accordance with the
equation

$2RCOCHBrR' + 2KOH =$
$$RCOCOR' + RCOCH_2R' + 2KBr + H_2O.$$
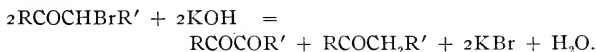
The relation between the amounts of mono- and diketone ob-
tained is constant but the total yield of these products varies
greatly because it depends upon conditions that are hard to
control. By adding a dilute alcoholic solution of potassium
hydroxide sufficiently slowly to a solution of the bromketone,
it is possible to get 95 per cent of the calculated amount of
the corresponding hydroxyl compound. The result is the
same when a stronger solution is added rapidly to a boiling
solution of the ketone, because, at this temperature, the re-
placement of bromine with hydroxyl is almost instantaneous.
The diketone is formed in quantity only when the solution
is alkaline; but as α-diketones are sensitive to bases, much of
the product may undergo condensation to quinone, or hy-
drolysis to acid and aldehyde unless the concentration of the
base is small and the temperature low.

Pure α-oxyketones are easily obtained by treating the brom
compounds with anhydrous potassium acetate, and saponi-
fying the acetates by boiling with water and barium carbon-
ate. As treatment with potassium hydroxide, under the con-
ditions most favorable for the formation of diketones from
bromketones, gives neither diketones nor their condensation
products it seems unlikely that the oxyketones are interme-
diate products in the reaction under consideration.

EXPERIMENTAL PART.

I. Experiments with α-Brompropio-p-bromphenone.

This ketone was obtained from brombenzene and α-brom-
propiophenone by the Friedel and Crafts reaction. By using

carbon disulphide as a medium, and excess of active aluminium chloride, and exposing to sunlight to complete the reaction, it was possible to get approximately 95 per cent of the calculated amount of the pure ketone. With dry gasoline as a medium the amount of crude product was almost the same, but the loss in purifying was much greater so that the yield of pure ketone did not exceed 85 per cent.

Reaction with Potassium Hydroxide.—A solution obtained by dissolving potassium hydroxide in its own weight of water and diluting with 3 volumes of absolute alcohol was added, in portions of 10 cc., to a solution of 200 grams of the bromketone in the smallest possible quantity of cold absolute alcohol. The liquid was shaken vigorously, after each addition, until the temporary orange color disappeared, and the addition of hydroxide was stopped when this color persisted after shaking for 5 minutes. This required almost exactly one molecule of potassium hydroxide for one of ketone.

The liquid was acidified with acetic acid and distilled to remove most of the alcohol. The residue was then poured into water, the yellow oil dissolved in ether, washed with sodium carbonate, dried with fused sodium sulphate, and fractioned under diminished pressure.

The washings yielded 4.8 grams of an acid that after purification from alcohol melted at 251°. Analysis:

0.1769 gram substance gave 0.2700 gram CO_2 and 0.0414 gram H_2O.

	Calculated for $C_7H_5O_2Br$.	Found.
C	41.7	41.6
H	2.5	2.6

Analysis and melting point indicated that the substance was *p*-brombenzoic acid and this was confirmed by making the methyl ester, which melted at 74°.

The distillation under diminished pressure gave 102 grams of yellow distillate below 180°—the temperature at which the residue began to decompose with formation of water and rapid evolution of gas. The distillate, on cooling, deposited some more *p*-brombenzoic acid which was evidently formed

during the distillation. When this was removed the entire liquid distilled between 158°–162°. After repeated distillations the last fraction solidified in a freezing mixture. The solid was separated by reverse filtration and crystallized from ligroin. Analysis:

I. 0.1635 gram substance gave 0.2870 gram CO_2 and 0.0465 gram H_2O.

II. 0.2133 gram substance gave 0.3746 gram CO_2 and 0.0614 gram H_2O.

| | Calculated for $C_9H_7O_2Br$. | Found. | |
		I.	II.
C	47.57	47.9	47.9
H	3.10	3.1	3.2

The molecular weight was determined in benzene ($K = 50$).

Solvent, grams.	Substance, gram.	Depression of freezing-point.	Molecular weight.
11.9	0.2595	0.505	216
11.9	0.4105	0.800	216
11.9	0.5605	1.076	220
Calculated for $C_9H_7O_2Br$,			227

When the substance was boiled for two hours with an alcoholic solution of hydroxylamine it formed a sparingly soluble dioxime that separated from the hot solution in small lustrous prisms melting at 237°. As it is sparingly soluble in alcohol and ether it was purified by recrystallization from amyl alcohol. Analysis:

I. 0.2241 gram substance gave 0.3476 gram CO_2 and 0.0716 gram H_2O.

II. 0.4180 gram substance gave 41.2 cc. nitrogen at 20° and 754 mm.

| | Calculated for $C_9H_9O_2N_2Br$. | Found. | |
		I.	II.
C	42.02	42.3	..
H	3.50	3.6	..
N	10.90	....	11.2

These results show that the yellow solid is not an unsaturated ketone but *p*-bromphenylmethyl diketone—a mixed α-diketone similar to those made by von Pechmann.

p-Bromphenylmethyl diketone, $BrC_6H_4COCOCH_3$, is a yellow solid melting at 48°. It is almost insoluble in water, but

readily soluble in all common organic solvents. The pure dry solid is stable in the air, but in solution and in the presence of impurities, the substance rapidly combines with oxygen and water, and passes into p-brombenzoic acid and acetic acid. In contact with strong aqueous potassium hydroxide it is hydrolyzed to p-brombenzoic acid and acetaldehyde, while strong alcoholic potassium hydroxide gives rise to colored condensation products—probably quinones similar to those obtained by von Pechmann from benzoylacetyl.

The *phenylhydrazone* was obtained by boiling an alcoholic solution of the ketone with one equivalent of phenylhydrazine. It is sparingly soluble in alcohol and separates in very thin yellow plates that melt at 199°. Analysis:

0.2467 gram substance gave 0.5088 gram CO_2 and 0.0925 gram H_2O.

	Calculated for $C_{15}H_{13}ON_2Br$.	Found.
C	56.7	56.3
H	4.1	4.2

As p-bromphenylmethyl diketone has carbonyl adjoining a methyl group it readily combines with bisulphites. The addition product with sodium bisulphite is a white, crystalline solid, sparingly soluble in water, insoluble in absolute alcohol. It yields pure diketone when it is suspended in dilute sulphuric acid and distilled with steam. It can, therefore, be used not only for removing all of the diketone from the mixture of products obtained by the action of potassium hydroxide on α-brom-p-brompropiophenone but also for determining the amount of diketone formed. In the experiment described above, for example, all the distillates and filtrates were collected, the solvents removed, and the residue shaken for two hours with excess of a saturated solution of the bisulphite. The resulting paste was filtered, the solid washed—first with a solution of bisulphite, then with a small quantity of absolute alcohol, and finally with ether. The ethereal extract of the filtrate was yellow, as was also the residue left after removing alcohol and ether, but tests with phenylhydrazine and potassium hydroxide showed that all of the diketone

had been removed. By repeated distillation of this residue, under diminished pressure, it was separated into two pure products—a colorless solid melting at 48° and a pale yellow liquid boiling at 169° under 15 mm.

The solid was *p*-brompropiophenone. This was established by comparison with a specimen made from propionyl chloride and brombenzene. It has almost the same boiling point as *p*-bromphenylmethyl diketone and it is equally volatile with steam. When boiled with an alcoholic solution of hydroxylamine it forms an oxime that is readily soluble in alcohol. This oxime separates from hot solutions in long needles that become opaque after removal from the liquid, from cold solutions in thick plates that remain transparent. Both forms melt at 89°. This is 5° higher than the melting point found by Collet, but the analysis shows that the substance was pure. Analysis:

0.2351 gram substance gave 0.4077 gram CO_2 and 0.0878 gram H_2O.

	Calculated for $C_9H_{10}ONBr.$	Found.
C	47.37	47.3
H	4.39	4.1

The pale yellow oil boiling at 169° (16 mm.) gave the following analytical results:

I. 0.2137 gram substance gave 0.3706 gram CO_2 and 0.0798 gram H_2O.

II. 0.2360 gram substance gave 0.4076 gram CO_2 and 0.2350 gram H_2O.

	Calculated for $C_9H_9O_2Br.$	Found. I.	II.
C	47.16	47.3	47.4
H	4.00	4.1	4.2

The substance is *α-oxypropio-p-bromphenone*,

$$BrC_6H_4COCHOHCH_3.$$

This was established by the following method of preparation: *p-Brombenzoylethyl acetate*, $BrC_6H_4COCH(OCOCH_3)CH_3$, was made by boiling a solution of *α-brompropio-p-bromphenone* in absolute alcohol with excess of fused potassium

acetate for two hours. It is a very viscous, colorless liquid that boils at 183°–185° (16 mm.). Analysis:

0.1342 gram substance gave 0.2390 gram CO_2 and 0.0513 gram H_2O.

	Calculated for $C_{11}H_{11}O_3Br.$	Found.
C	48.70	48.57
H	4.06	4.24

For the purpose of hydrolysis, 20 gram portions of the acetate were boiled for 4 hours with 1 liter of water and excess of freshly precipitated barium carbonate. The resulting liquid was dissolved in ether and the solution dried and distilled under diminished pressure. The product boiled at 169°–170° (16 mm.) and the distillate was in every way identical with the third substance obtained by the action of potassium hydroxide on α-brompropio-p-bromphenone. The oxyketone is a pale yellow, viscous liquid that does not solidify in a freezing mixture. It is less volatile with steam than the two other products of the reaction and it boils at a little higher temperature. As it is readily oxidized by potassium permanganate, it is easy to remove it from the mixture with p-brompropiophenone that is left after treating the entire product of the reaction with bisulphite. It was possible, therefore, to make a fairly accurate quantitative determination of all three of the products.

The procedure was as follows: Two hundred and fifty grams of bromketone were treated with potassium hydroxide and the product distilled under diminished pressure as before. This gave 130 grams of oil, boiling below 180° (18 mm.), and free from p-brombenzoic acid. The oil was shaken with 1 liter of a saturated solution of sodium bisulphite for 6 hours. The liquid was then drawn off with the pump, and the solid washed with absolute alcohol and ether. The addition product yielded 51 grams of pure, solid, diketone when suspended in dilute sulphuric acid and distilled with steam. The filtrate from the bisulphite addition product was extracted with ether, then acidified and likewise distilled with steam, but yielded less than a gram more of diketone.

The ethereal extract was dried, the ether and alcohol removed by distillation, and the residue oxidized by shaking with an aqueous solution of potassium permanganate. This left 50.5 grams of *p*-brompropiophenone which was separated by distillation with steam. Finally, the oxides of manganese were dissolved with sodium bisulphite and sulphuric acid, and the solution extracted with ether. The ether, on evaporation, deposited 26.8 grams of *p*-brombenzoic acid—representing 23.5 grams of oxyketone. The amount of diketone is somewhat less than 1 molecule for 1 molecule of monoketone, but this is to be expected because the latter is unstable in the presence of acids and bases.

II. *Experiments with α-Brompropiophenone.*

The reaction was carried out like that with the *p*-brom derivative but as the ketone is readily soluble in alcohol more concentrated solutions could be used. Distillation under diminished pressure gave 210 grams of yellow oil boiling below 140° (16 mm.), from 500 grams of bromketone. This oil contained no phenylvinyl ketone; it did not combine with bromine while the unsaturated ketone combines with it as readily as does benzalacetone. Special tests showed that the oil contained phenylmethyl diketone, propiophenone, and α-oxypropiophenone. The oxyketone was not separated from the mixture but its presence is shown by the fact that the oil contains a pale yellow substance that does not combine with bromine or acid sulphites, but is oxidized by aqueous permanganate to benzoic and acetic acids. A quantitative determination carried out as described in the last experiment with α-brompropio-*p*-bromphenone showed that 200 grams of the mixture contained 82 grams of phenylmethyl diketone, 76 grams of propiophenone, and 42 grams of α-oxypropiophenone. The diketone was identified by its hydrazone, melting at 144°, and its dioxime, melting at 229°. The propiophenone was mixed with a specimen on hand, the mixture solidified by cooling in a freezing mixture, and then allowed to melt; the melting point was the same as that of the components.

III. Experiments with α-Bromisovaleryl-p-bromphenyl Ketone.

This ketone, $BrC_6H_4COCHBrCH(CH_3)_2$, was made from brombenzene and α-bromisovaleryl bromide by the Friedel and Crafts reaction. Although the procedure was the same as that which had given excellent results with other acid bromides, the yield in this case was much smaller—210 grams from 250 grams of bromide. The ketone crystallizes in needles melting at 49°. It is readily soluble in alcohol and ether, moderately in low-boiling ligroin and methyl alcohol. Analysis:

0.1815 gram substance gave 0.2729 gram CO_2 and 0.0359 gram H_2O.

	Calculated for $C_{11}H_{12}OBr_2$.	Found.
C	41.25	41.01
H	3.11	3.30

The reaction between potassium hydroxide and this ketone gives no products that do not boil without decomposition under diminished pressure, because the resulting diketone does not have the group necessary for condensation to quinone. The entire product distilled between 165°–172° (16 mm.). Preliminary tests showed that the yellow distillate contained substances analogous to those obtained from other bromketones. In order to test for unsaturated ketone, some of the oil was dissolved in carbon tetrachloride, the solution cooled to 0° and treated with a few drops of bromine dissolved in the same solvent. The color of bromine remained for an hour. As both mesityl oxide and phenylvinyl ketone under these conditions combine with bromine as fast as it is added, this result proves the absence of unsaturated ketone. The presence of diketone was shown by the oxidation in contact with air, and that of monoketone by oxidation with permanganate and distillation with steam.

As none of the components of the mixture combines with acid sulphites it was necessary to undertake their separation by distillation. Fractional distillation under diminished pressure proved useless; analyses made after 5 distillations showed that the first and last fractions had almost the same composi-

tion. Distillation with steam gave more promising results as the analyses showed that the diketone accumulated in the first fraction. After 6 distillations, carried out like ordinary fractional distillations except that the fractions were collected by quantity instead of boiling point, the first fraction gave results agreeing closely with those calculated for the diketone.

I. 0.1821 gram substance gave 0.3438 gram CO_2 and 0.0737 gram H_2O.

II. 0.2276 gram substance gave 0.4297 gram CO_2 and 0.0920 gram H_2O.

	Calculated for $C_{11}H_{11}O_2Br$.	I.	II.
		Found.	
C	51.76	51.49	51.55
H	4.32	4.5	4.55

The yellow liquid had a constant boiling point, 168°–169° (15 mm.), but it was impossible to prove that it represented a pure substance. As only acid products were left after oxidation with aqueous permanganate it was certainly free from *p*-bromisovalerophenone; but it may have contained the α-hydroxy derivative of this ketone in quantities too small for recognition by analysis. The *dioxime* was obtained by boiling the ketone with an alcoholic solution of hydroxylamine. It separated from alcohol in fine needles melting at 229°. It is moderately soluble in alcohol and ether, insoluble in benzene and ligroin.

Analysis:

0.3855 gram substance gave 35 cc. nitrogen at 22° and 754 mm.

	Calculated for $C_{11}H_{13}O_2N_2Br$.	Found.
N	9.82	10.2

p-Bromisovalerophenone, $BrC_6H_4COCH_2CH(CH_3)_2$.—The last three fractions obtained by the steam distillation were combined and shaken with a cold aqueous solution of potassium permanganate. This destroyed both the oxy- and the diketone. The unoxidized product was separated by distillation with steam. The ketone solidified in the receiver. After one crystallization from methyl alcohol it melted sharply at 48°.

It crystallizes in large plates that are readily soluble in the common organic solvents.

Analysis:

0.1708 gram substance gave 0.3415 gram CO_2 and 0.0845 gram H_2O.

	Calculated for $C_{11}H_{13}OBr$.	Found.
C	54.78	54.5
H	5.39	5.5

The *oxime*, made by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and excess of potassium hydroxide, crystallizes in needles and melts at 91°–92°. It is readily soluble in alcohol and ether, sparingly in ligroin, insoluble in water.

Analysis:

0.1622 gram substance gave 0.3045 gram CO_2 and 0.0841 gram H_2O.

	Calculated for $C_{11}H_{14}ONBr$.	Found.
C	51.56	51.2
H	5.47	5.8

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  February, 1909.

NOTE ON THE PREPARATION AND THE USE OF ASBESTOS FOR GOOCH CRUCIBLES.

BY PHILIP ADOLPH KOBER.

Although asbestos has been used for Gooch crucibles for some time, yet no standard method of preparation has been adopted. Filter papers for similar purposes, of definite and uniform grades, have been on the market for years. The adoption of a standard, either of asbestos, or of a method for preparing the same, would hasten the day of a more general use of the Gooch crucible.

It is the object of this paper, first, to describe a convenient and quick method of preparation of asbestos, and secondly, to give the possible uses of asbestos, so prepared.

Preparation.—Crude asbestos, obtained from the supply

house, is directly[1] purified by digestion in a strong solution of nitro-hydrochloric acid at a low heat for several hours. After filtering off the acid and washing with distilled water a few times through a Buchner funnel, the asbestos, which at this stage contains mostly large fibres, is transferred to a bottle or cylinder with sufficient water to make a good suspension (2–10 grams per liter). Then, as suggested by Folin,[2] a strong air current is passed through the suspension for a few minutes (5 to 10 min.).

This agitation is sufficient to tear the crude material into fine shreds, but is not quite sufficient to produce a pulp, emulsive in appearance.

To produce an emulsive-looking pulp, a quality that yields fine asbestos paper, a further treatment is necessary. This consists essentially in filtering the suspension of asbestos, after agitation, through a Buchner funnel (10 cm.) with the aid of strong suction, the perforations of the funnel being kept open by stirring with a glass rod. The filtrate should not contain any large fibres. Large quantities of purified asbestos can thus be prepared in twenty minutes without much manual labor.

Use.—Asbestos pulp, prepared as described above and diluted to about 0.1 per cent, can be used almost as a real solution. After thorough shaking for a few minutes, the amount obtainable by volumetric measurement is, for most analytical filtrations and determinations, a constant quantity. To put this statement in other words, a suspension of asbestos can be obtained which makes it easily possible to control the weight of the asbestos mat. Furthermore, by using the same volume of asbestos solution, and assuming that the crucible does not change materially in weight through use, a Gooch crucible of constant weight is practically obtained.

With an ordinary 2½ liter bottle, having a suitable pipette attached through the stopper, mats were obtained which gave the results shown in columns 1 and 2, when the porcelain crucible (12–14 grams) was weighed before and after the addi-

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[1] Cutting or scraping of dry fibre is in this method unnecessary.
[2] Folin: J. Biol. Chem., **1**, 149 (1906).

tion of the asbestos. Substituting an automatic[1] pipette for
an ordinary one, mats were obtained which, when removed
as asbestos paper, dried, ignited, and weighed, gave the results
shown in columns 3 and 4.

Ordinary Pipette.		*Automatic Pipette.*	
1. Weight.	2. Difference.	3. Weight.	4. Difference.
0.0143	0.00004	0.01535	0.00007
0.0144	0.00014	0.01520	0.00008
0.0142	0.00006	0.01520	0.00008
0.0141	0.00016	0.01535	0.00007
0.0144	0.00014	0.01535	0.00007
0.0142	0.00006	0.01510	0.00018
0.01426 Av.	0.00010 Av.	0.01535	0.00007
		0.01535	0.00007
		0.01528 Av.	0.000086 Av.

A quantitative control of the asbestos is advantageous,
as it permits not only the elimination, for technical work, of the
first weighing of the crucible, and, for more accurate work,
the postponement of the weighing until after the filtration,
but also the substitution of a fresh mat for an old one which
for some reason or other filters too slowly.[2]

The details for making the mats, the weights of which are
given above, are as follows: To the crucible, fitted directly,
or by an adapter, to a suction flask, are added 15 cc. of 0.1
per cent asbestos. After a few drops have filtered through,
a slight suction is applied, and maintained until the mat has
been formed and all the water has been filtered. A very strong
vacuum is maintained for a minute or more, and the asbestos
is then washed with several portions of distilled water. After
the suction has been interrupted and the filtrate *refiltered*
and washed, the crucible is ready for use.

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[1] The outlet of this pipette was 0.5 cm. in width.

[2] It sometimes occurs in making many determinations, especially in physiological
chemistry, that a mat will cease to filter in the middle of a filtration.

THE CONDUCTIVITY OF SOLUTIONS OF LITHIUM NITRATE IN TERNARY MIXTURES OF ACETONE, METHYL ALCOHOL, ETHYL ALCOHOL, AND WATER; TOGETHER WITH THE VISCOSITY AND FLUIDITY OF THESE MIXTURES.

[TENTH COMMUNICATION.]

By HARRY C. JONES AND EDWARD G. MAHIN.

A large amount of work has been done with the object of learning something about the electrochemistry of organic solvents, and of binary mixtures of these liquids. This is especially true with regard to the relations existing between conductivity and viscosity of solutions in such solvents. A full account of the work which has been done in this laboratory has been published as a monograph by Jones[1] and coworkers, and the electrochemistry of nonaqueous solvents has been extensively discussed by Carrara.[2]

In the following pages are recorded the results of a few preliminary experiments, which were made with the object of determining whether any essentially new principles were to be discovered by increasing the number of components of a solvent mixture from two to three. It would be, of course, impossible to predict whether or not the mutual action of three solvents upon each other would be the average action of the three possible pairs of components. No extensive study of this matter has, as yet, been made. We have measured the viscosity of ternary mixtures of water, methyl alcohol, ethyl alcohol, and acetone; and the conductivity of lithium nitrate in these mixtures. The materials, apparatus, and method of making the measurements were essentially the same as outlined in earlier articles. The following example will serve to indicate the method of designating the solvent mixtures: "Acetone (75 per cent Methyl Alcohol and Water)" indicates a mixture of solvents made by adding stated amounts (per cent by volume) of acetone to a mixture of methyl alcohol

[1] Carnegie Institution Pub., No. 80 (1907).
[2] Ahren's Sammlung, **12**, No. 11 (1908).

and water which contains 75 per cent, by volume, of methyl alcohol.

Table I.—*Conductivity of Lithium Nitrate in Acetone (25 Per Cent Methyl Alcohol and Water).*

	\% Acetone. At 0°				
V.	0 %.	25 %.	50 %.	75 %.	100 %.
10	27.26	23.08	23.13	25.80	9.67
50	29.41	24.50	26.60	33.10	14.07
100	30.11	26.07	27.37	35.50	18.1
200	31.06	. . .	. . .	38.22	23.8
400	31.35	30.18	28.91	40.54	30.6
800	31.62	31.85	29.27	42.03	43.4
1600	32.16	. . .	29.73	43.21	55.3
	At 25°				
10	56.46	48.07	44.78	40.31	10.87
50	61.51	51.65	51.89	55.29	15.64
100	63.53	55.43	53.88	59.78	19.5
200	65.72	. . .	. . .	64.80	25.3
400	66.41	64.05	57.42	68.85	32.4
800	66.94	66.63	58.21	71.78	45.5
1600	68.20	. . .	58.40	73.16	59.8

Table II.—*Conductivity of Lithium Nitrate in Acetone (50 Per Cent Methyl Alcohol and Water).*

	\% Acetone. At 0°				
V.	0 %.	25 %.	50 %.	75 %.	100 %.
10	21.86	22.54	25.15	28.09	9.67
50	23.91	25.55	29.57	37.62	14.07
100	24.79	26.57	31.08	41.25	18.1
200	25.37	27.11	32.55	44.28	23.8
400	25.47	28.70	34.14	47.31	30.6
800	26.10	28.62	34.17	48.52	43.4
1600	26.94	30.26	35.35	50.40	55.3
	At 25°.				
10	44.58	43.79	44.42	42.77	10.87
50	49.41	50.18	53.11	58.37	15.64
100	51.44	52.32	55.90	64.40	19.5
200	52.79	53.67	59.02	69.82	25.3
400	53.10	55.05	62.03	74.56	32.4
800	54.32	56.50	64.35	77.97	45.5
1600	56.50	57.95	64.41	80.10	59.8

Table III.—*Conductivity of Lithium Nitrate in Acetone (75 Per Cent Methyl Alcohol and Water).*

V.	0 %.	25 %.	At 0° % Acetone. 50 %.	75 %.	100 %.
10	24.16	26.32	29.56	31.55	9.67
50	27.56	30.99	36.94	44.86	14.07
100	28.67	32.99	38.90	50.16	18.1
200	29.60	34.11	41.90	55.20	23.8
400	29.82	34.75	42.96	58.80	30.6
800	30.62	35.30	44.31	61.75	43.4
1600	31.45	36.71	45.45	64.84	55.3
			At 25°.		
10	43.06	44.63	46.21	43.16	10.87
50	49.58	53.29	58.56	63.32	15.64
100	51.96	56.06	62.36	71.28	19.5
200	53.80	59.20	67.37	79.26	25.3
400	54.63	60.23	69.32	84.82	32.4
800	55.72	61.24	71.51	89.78	45.5
1600	58.06	63.88	73.49	94.22	59.8

Table IV.—*Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Methyl Alcohol, and Water. In Acetone (75 Per Cent Methyl Alcohol and Water).*

V.	0 %.	25 %.	At 0° % Acetone. 50 %.	75 %.	100 %.
10	0.0428	0.0433	0.0374	0.0225	0.0049
50	0.0437	0.0443	0.0380	0.0268	0.0045
100	0.0444	0.0450	0.0387	0.0273	0.0031
200	0.0446	....	....	0.0278	0.0025
400	0.0447	0.0449	0.0394	0.0279	0.0023
800	0.0447	0.0437	0.0395	0.0283	0.0019
1600	0.0448	....	0.0386	0.0277	0.0032

In Acetone (50 Per Cent Methyl Alcohol and Water).

10	0.0416	0.0377	0.0314	0.0209	See above
50	0.0427	0.0385	0.0318	0.0221	"
100	0.0430	0.0388	0.0319	0.0224	"
200	0.0432	0.0391	0.0325	0.0231	"
400	0.0434	0.0367	090327	0.0230	"
800	0.0433	0.0390	0.0326	0.0243	"
1600	0.0439	0.0366	0.0326	0.0236	"

Table IV.—(Continued.)

In Acetone (75 Per Cent Methyl Alcohol and Water).

10	0.0313	0.0278	0.0225	0.0151	See above
50	0.0320	0.0288	0.0234	0.0165	"
100	0.0325	0.0290	0.0241	0.0168	"
200	0.0327	0.0294	0.0243	0.0174	"
400	0.0333	0.0292	0.0245	0.0177	"
800	0.0328	0.0294	0.0246	0.0182	"
1600	0.0338	0.0296	0.0247	0.0181	"

Table V.—Conductivity of Lithium Nitrate in Acetone (25 Per Cent Ethyl Alcohol and Water).

	At 0° % Acetone.				
V.	0 %.	25 %.	50 %.	75 %.	100 %.
10	19.66	18.74	20.71	23.93	9.67
50	21.03	20.44	23.64	30.73	14.07
100	21.51	21.05	24.61	33.31	18.1
200	22.03	21.70	25.46	35.20	23.8
400	22.20	22.15	25.78	36.74	30.6
800	22.48	22.04	26.38	37.96	43.4
1600	24.54	22.83	26.69	40.74	55.3
			At 25°.		
10	46.70	42.51	41.31	39.75	10.87
50	51.11	47.25	47.93	52.10	15.64
100	52.37	48.76	50.12	56.84	19.5
200	54.00	50.42	52.19	60.51	25.3
400	54.60	51.76	52.93	63.21	32.4
800	55.39	51.62	54.17	65.59	45.5
1600	58.59	52.96	54.78	70.11	59.8

Table VI.—Conductivity of Lithium Nitrate in Acetone (50 Per Cent Ethyl Alcohol and Water).

	At 0° % Acetone.				
V.	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.53	15.98	19.85	23.80	9.67
50	13.57	17.89	23.62	32.49	14.07
100	14.02	18.63	25.13	35.90	18.1
200	14.42	19.21	26.13	38.84	23.8
400	14.60	. . .	26.98	39.67	30.6
800	14.88	19.33	. . .	43.56	43.4
1600	14.88	20.56	30.23	46.13	55.3

Table VI.—(Continued.)

			At 25°.		
10	31.82	34.54	36.95	36.77	10.87
50	35.34	39.43	44.64	51.27	15.64
100	36.56	41.23	47.69	58.06	19.5
200	37.88	42.64	49.88	62.36	25.3
400	38.31	. . .	51.71	63.83	32.4
800	38.96	44.15	. . .	68.75	45.5
1600	39.35	45.56	53.86	71.67	59.8

Table VII.—*Conductivity of Lithium Nitrate in Acetone (75 Per Cent Ethyl Alcohol and Water).*

	At 0° % Acetone.				
V.	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.01	15.84	20.41	23.29	9.67
50	13.80	19.00	26.84	35.29	14.07
100	14.48	20.21	29.06	40.41	18.1
200	15.14	20.92	31.76	44.80	23.8
400	15.41	21.67	32.70	48.43	30.6
800	15.76	22.52	35.55	51.38	43.4
1600	16.10	22.56	35.20	54.01	55.3
	At 25°.				
10	25.56	29.66	33.32	32.59	10.87
50	29.91	36.32	44.69	50.39	15.64
100	31.64	38.85	48.68	58.35	19.5
200	33.12	40.44	53.90	65.72	25.3
400	33.90	42.11	55.52	71.59	32.4
800	34.88	41.91	57.32	76.39	45.5
1600	35.85	43.97	60.54	81.28	59.8

Table VIII.—*Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Ethyl Alcohol, and Water. In Acetone (25 per cent Ethyl Alcohol and Water).*

	At 0° % Acetone.				
V.	0 %.	25 %.	50 %.	75 %.	100 %.
10	0.0550	0.0507	0.0398	0.0265	0.0049
50	0.0572	0.0524	0.0411	0.0291	0.0045
100	0.0574	0.0526	0.0414	0.0282	0.0031
200	0.0581	0.0530	0.0420	0.0287	0.0025
400	0.0584	0.0535	0.0421	0.0288	0.0023
800	0.0585	0.0537	0.0422	0.0290	0.0019
1600	0.0555	0.0528	0.0421	0.0288	0.0032

Table VIII.—(Continued.)

In Acetone (50 Per Cent Ethyl Alcohol and Water).

10	0.0614	0.0464	0.0341	0.0218	See above
50	0.0642	0.0482	0.0356	0.0231	"
100	0.0643	0.0485	0.0359	0.0247	"
200	0.0650	0.0488	0.0364	0.0242	"
400	0.0649	. . . . .	0.0367	0.0244	"
800	0.0647	0.0491	. . . .	0.0231	"
1600	0.0658	0.0486	0.0313	0.0222	"

In Acetone (75 Per Cent Ethyl Alcohol and Water).

10	0.0451	0.0349	0.0253	0.0160	See above
50	0.0467	0.0365	0.0267	0.0171	"
100	0.0474	0.0369	0.0270	0.0177	"
200	0.0475	0.0373	0.0278	0.0187	"
400	0.0480	0.0377	0.0278	0.0192	"
800	0.0485	0.0380	0.0283	0.0194	"
1600	0.0491	0.0379	0.0288	0.0202	"

Table IX.—Conductivity of Lithium Nitrate in Methyl Alcohol (25 Per Cent Ethyl Alcohol and Water).

	At 0°				
	% Methyl Alcohol.				
V.	0 %.	25 %.	50 %.	75 %.	10? %.
10	19.66	17.76	19.50	24.35	37.62
50	21.03	19.11	21.65	28.13	48.31
100	21.51	19.89	22.46	29.68	52.0
200	22.03	20.19	22.76	31.76	55.1
400	22.20	20.57	23.08	31.32	56.8
800	22.48	20.63	23.39	32.19	59.6
1600	24.54	21.09	23.34	32.73	61.9
			At 25°.		
10	46.70	40.13	39.04	41.67	51.31
50	51.11	44.13	44.05	48.85	67.2
100	52.37	45.97	45.81	51.49	72.6
200	54.00	46.48	46.53	53.73	76.8
400	54.60	47.86	47.35	53.94	80.0
800	55.39	48.10	47.96	56.14	83.7
1600	58.59	49.72	47.92	57.59	86.7

Table X.—Conductivity of Lithium Nitrate in Methyl Alcohol (50 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Methyl Alcohol.				
	0 %.	25 %.	50 %.	75 %.	100 %,
10	12.53	15.35	19.19	25.18	37.62
50	13.57	16.96	21.95	30.04	48.31
100	14.02	17.61	22.87	31.69	52.0
200	14.42	18.02	23.75	32.97	55.1
400	14.60	18.41	24.61	34.18	56.8
800	14.88	18.60	24.98	34.57	59.6
1600	14.88	19.50	25.15	35.48	61.9
			At 25°.		
10	31.82	33.24	36.13	41.18	51.31
50	35.34	37.35	41.91	49.48	67.2
100	36.56	39.10	43.87	52.36	72.6
200	37.88	40.08	45.72	54.91	76.8
400	38.31	41.57	47.44	57.06	80.0
800	38.96	41.63	48.06	57.67	83.7
1600	39.35	43.82	48.53	59.61	86.7

Table XI.—Conductivity of Lithium Nitrate in Methyl Alcohol (75 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Methyl Alcohol.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.01	15.46	20.00	26.46	37.62
50	13.80	17.96	23.82	32.38	48.31
100	14.48	19.03	25.22	34.69	52.0
200	15.14	19.72	26.11	36.17	55.1
400	15.41	20.32	26.77	37.46	56.8
800	15.76	20.55	27.15	38.51	59.6
1600	16.10	20.82	27.54	39.55	61.9
			At 25°.		
10	25.56	29.28	34.09	40.91	51.31
50	29.91	34.77	41.20	50.50	67.2
100	31.64	36.93	43.89	54.35	72.6
200	33.12	38.41	45.52	56.89	76.8
400	33.90	39.81	46.82	59.08	80.0
800	34.88	40.52	47.51	60.86	83.7
1600	35.85	41.34	48.39	62.84	86.7

Table XII.—Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Methyl Alcohol, Ethyl Alcohol, and Water.

In Methyl Alcohol (25 Per Cent Ethyl Alcohol and Water).

	% Methyl Alcohol.				
V.	0 %.	25 %.	50 %.	75%.	100 %.
10	0.0550	0.0504	0.0400	0.0284	0.0145
50	0.0572	0.0524	0.0414	0.0295	0.0157
100	0.0574	0.0524	0.0415	0.0294	0.0155
200	0.0581	0.0521	0.0417	0.0276	0.0147
400	0.0584	0.0530	0.0420	0.0289	0.0172
800	0.0585	0.0532	0.0420	0.0298	0.0162
1600	0.0555	0.0542	0.0422	0.0301	0.0160

In Methyl Alcohol (50 Per Cent Ethyl Alcohol and Water).

10	0.0614	0.0466	0.0353	0.0254	See above
50	0.0642	0.0481	0.0364	0.0258	"
100	0.0643	0.0488	0.0367	0.0262	"
200	0.0650	0.0492	0.0370	0.0266	"
400	0.0649	0.0503	0.0371	0.0267	"
800	0.0647	0.0495	0.0365	0.0267	"
1600	0.0658	0.0499	0.0372	0.0272	"

In Methyl Alcohol (75 Per Cent Ethyl Alcohol and Water).

10	0.0451	0.0358	0.0282	0.0219	See above
50	0.0467	0.0374	0.0292	0.0224	"
100	0.0474	0.0376	0.0297	0.0227	"
200	0.0475	0.0379	0.0297	0.0229	"
400	0.0480	0.0383	0.0300	0.0231	"
860	0.0485	0.0388	0.0300	0.0232	"
1600	0.0491	0.0394	0.0303	0.0235	"

Table XIII.—Viscosity and Fluidity of Mixtures of Acetone, Methyl Alcohol, and Water.

Acetone (25 Per Cent Methyl Alcohol and Water).

% Acetone.	η 0°.	η 25°.	ϕ 0°.	ϕ 25°.	Temp. coef.
0	0.03286	0.01368	30.44	73.11	0.0561
25	0.03386	0.01428	29.53	70.04	0.0549
50	0.02597	0.01209	38.50	82.75	0.0460
75	0.01310	0.00751	76.36	133.22	0.0303
100	0.00429	0.00346	233.21	288.95	0.0096

Table XIII.—(Continued.)

Acetone (50 Per Cent Methyl Alcohol and Water).

0	0.03586	0.01541	27.81	64.89	0.0531
25	0.02850	0.01340	35.09	74.65	0.0451
50	0.01926	0.01514	51.92	99.96	0.0371
75	0.00984	0.00620	101.63	161.40	0.0235
100	0.00429	0.00346	233.21	288.95	0.0096

Acetone (75 Per Cent Methyl Alcohol and Water).

0	0.02461	0.01253	41.64	79.84	0.0463
25	0.01824	0.00990	54.81	101.06	0.0338
50	0.01203	0.00726	83.10	137.79	0.0263
75	0.00705	0.00491	141.76	203.85	0.0175
100	0.00429	0.00346	233.21	288.95	0.0096

Table XIV.—Viscosity and Fluidity of Mixtures of Acetone, Ethyl Alcohol, and Water.

Acetone (25 Per Cent Ethyl Alcohol and Water.)

% Acetone.	η 0°.	η 25°.	ϕ 0°.	ϕ 25°.	Temp. coef.
0	0.05111	0.01745	19.57	57.30	0.0770
25	0.04329	0.01644	23.10	60.83	0.0653
50	0.02856	0.01288	35.02	67.63	0.0487
75	0.01356	0.00770	73.74	129.88	0.0305
100	0.00429	0.00346	233.21	288.95	0.0096

Acetone (50 Per Cent Ethyl Alcohol and Water).

0	0.06949	0.02298	14.39	43.51	0.0643
25	0.04152	0.01693	24.09	79.05	0.0580
50	0.02284	0.01123	43.78	89.05	0.0414
75	0.01047	0.00648	95.54	154.41	0.0246
100	0.00429	0.00346	233.21	288.95	0.0096

Acetone (75 Per Cent Ethyl Alcohol and Water).

0	0.04826	0.01983	20.72	50.41	0.0573
25	0.02807	0.01341	35.63	74.56	0.0437
50	0.01529	0.00853	65.41	117.21	0.0317
75	0.00935	0.00637	106.93	156.87	0.0177
100	0.00429	0.00346	233.21	288.95	0.0096

Table XV.—Viscosity and Fluidity of Mixtures of Methyl Alcohol, Ethyl Alcohol, and Water.

Methyl Alcohol (25 Per Cent Ethyl Alcohol and Water).

% Acetone.	η 0°.	η 25°.	ϕ 0°.	ϕ 25°.	Temp. coef.
0	0.05111	0.01745	19.57	57.30	0.0770
25	0.04851	0.01862	20.61	53.70	0.0642
50	0.03804	0.01702	26.29	58.76	0.0493
75	0.02198	0.01160	45.49	86.24	0.0358
100	0.00857	0.00583	116.71	171.60	0.0176

Methyl Alcohol (50 Per Cent Ethyl Alcohol and Water).

0	0.06949	0.02298	14.39	43.51	0.0643
25	0.04919	0.01994	20.33	50.14	0.0587
50	0.03086	0.01481	32.41	67.52	0.0433
75	0.01928	0.01083	51.88	92.34	0.0311
100	0.00857	0.00583	116.71	171.60	0.0176

Methyl Alcohol (75 Per Cent Ethyl Alcohol and Water).

0	0.04826	0.01983	20.72	50.41	0.0573
25	0.03468	0.01614	28.83	61.97	0.0461
50	0.02337	0.01216	42.86	82.23	0.0369
75	0.01477	0.00880	67.70	113.62	0.0271
100	0.00857	0.00583	116.71	171.60	0.0176

From the results thus far obtained, it would seem that the viscosity and conductivity values in ternary mixtures are about what might be expected from the behavior of solutions in binary solvent mixtures. A series of experiments with a salt, such as potassium iodide, which shows no abnormality in any of the single solvents, would make possible a more exact comparison of experimental with calculated values. More extensive work along these lines, as well as further investigations in binary mixtures, is now in progress in this laboratory.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1908.

OBITUARY.

JULIUS THOMSEN.

By the death, on February 13th, of Julius Thomsen, less than two years after that of his French rival, Marcelin Berthelot, thermochemistry has lost the second of those two great

men to whose long and fruitful labors it owes chiefly its present important position in our science. Although Thomsen never showed the many-sidedness of Berthelot, did not introduce as many improvements, perhaps, in the methods of thermochemical investigation, yet his results are, in general, far more accurate and reliable. His book, "Thermochemische Untersuchungen," contains the most important thermochemical data on record, and the services he has rendered to science are incalculable.

Born in Copenhagen on February 18th, 1823, unlike most of his contemporaries, he never "wandered" and his native city can claim him wholly as her own, for here he studied, taught, and worked till the day of his death. Beginning as an assistant at the Polytechnik at the age of 21, he remained there till 1856, when he gave up his position to become a gauger. He soon resumed teaching, however, first as a lecturer in physics at the military "Hochschule," and, in 1866, as professor of chemistry at the University, a position which he held till 1891. The following year he became director of the Polytechnik.

From the first, Thomsen was an enthusiastic adherent of the theory of the unity and indestructibility of energy and as early as 1849 he attempted to determine the mechanical equivalent of electrical energy. He worked out some other problems in the field of electricity, among them being the discovery of a new galvanic element which met with considerable success, when, in 1849, a technical problem led him back to chemistry. A peculiar formation of wonderfully pure cryolite had been found in Greenland and it was Thomsen who, by the discovery of the cryolite soda process, made possible the economic utilization of this new mineral. After establishing this industry, he again turned to pure research, taking up, now, the heat changes involved in chemical reactions, and for over thirty years he worked tirelessly on this problem, making enormous numbers of measurements of the heats of solution, combination, and combustion of many compounds. Most of the results of his work were published in the *Berichte* of the German Chemical Society and in the *Journal für praktische Chemie*, and in 1882 were brought together in his monumental four-volume book, "Thermochemische Untersuchungen."

His work did not at once receive the attention and recognition which it merited. In 1877, however, the University of Upsala conferred upon him the degree of Doctor of Philosophy, and two years later that of Doctor of Medicine was given him

by the University of Amsterdam. In 1883 the Davy Medal was awarded to him. He was an honorary member of the German and American Chemical Societies.   C. A. R.

REVIEWS.

LES NOUVEAUTÉS CHIMIQUES POUR 1908. Nouveaux appareils de laboratoire. Méthodes nouvelles de recherches appliquées à la science et à l'industrie. Par CAMILLE POULENC, DOCTEUR ÈS SCIENCES. Avec 200 figures intercalées dans le texte. Paris: Librairie J. B. Baillière et Fils. 1908. pp. VIII + 354. Price, Fr. 4.

The appearance of former volumes of this annual publication has already been noted in THIS JOURNAL. The same general plan as in previous years has been followed by the author. Every one will find it well worth while to at least glance through this book, for a very large number of new forms of chemical apparatus is described.   C. A. R.

DECORATION OF METAL, WOOD, GLASS, ETC. A Book for Manufacturers, Mechanics, Painters, Decorators and all Workmen in the Fancy Trades. Edited by H. C. STANDAGE, Consulting Chemist. New York: John Wiley and Sons. 1908. pp. 228. Price, $2.00.

This book contains in compact form directions for making and using various preparations for decorating metals, wood, glass, etc. The editor seems to have covered the field very thoroughly.   C. A. R.

TEXT BOOK OF PHYSIOLOGICAL CHEMISTRY IN THIRTY LECTURES. By EMIL ABDERHALDEN. Translated by WILLIAM T. HALL and GEORGE DEFREN. New York: John Wiley & Sons. pp. XIII + 722. Price, $5.00, net.

An adequate translation of Prof. Abderhalden's text book is entitled to a very warm welcome. The German edition has taken its place in the front rank of the comparatively few text books on physiological chemistry which aim at anything like a philosophical treatment of the subject.

The lecture form of presentation and the mode of treatment in many ways recalls the older work of Bunge and it is interesting to note how enormously the scope of practical investigation and the general stock of facts has increased since the latter volume was published.

Perhaps the most novel portion of the book is contained in the two chapters entitled "Outlook," in which the reader will find much that is helpful and suggestive. Abderhalden develops in a logical fashion a chemical explanation for the conception of species and their maintenance, and shows how morphologically similar organs such as are found in the differ-

ent vertebrates have a chemical composition characteristic for each species and perhaps for each individual. It is interesting to contrast this opinion with diametrically opposite views of Cuvier, who wrote: "It is not in the substance that in plants and animals the identity of species is manifested, it is in the form."[1] Perhaps a compromise between these opposing ideas will be necessary in order to arrive at the truth.

With regard to the translation by Messrs. Hall and Defren, there is little to be said. On the whole, the translation is admirable and the system of spelling adopted for the various compounds is very satisfactory. Although the task of proofreading was shared by others than the translators, there is room for much improvement in this direction. The repeated use of the word "glucohemia" as the equivalent of "hyperglukämie" appears to be objectionable.

It is unfortunate that many comparatively glaring errors in matters of fact which have been exposed since the book was originally written should not have been corrected in the English edition. For example, it is stated in several places that tryptophane (indole-α-aminopropionic acid) yields skatolcarboxylic and skatolacetic acid through the action of putrefactive organisms, although it has been shown by Ellinger for a comparatively long time that these substances are indoleacetic and indolepropionic acids, respectively. Many other similar examples might be cited, but drawbacks such as these can only slightly detract from the general merit of so important a contribution to biochemical literature.

<div align="right">H. D. Dakin.</div>

Grundlagen und Ergebnisse der Pflanzenchemie. Nach der schwedischen Ausgabe bearbeitet von H. Euler, Professor der Chemie an der Universität Stockholm. Erster Teil: Das chemische Material der Pflanzen. Mit einer Abbildung im Text. Braunschweig: Druck und Verlag von Freidrich Vieweg und Sohn. 1908. pp. ix + 238. Price, M. 6, unbound; M. 7, bound.

Instead of taking up the entire compass of our knowledge of the constituents of the plant world, a method so admirably used in Czapek's *Biochemie der Pflanzen*, Euler considers in great detail the properties of a much smaller number of the more important classes of organic compounds and their changes.

In the second part, which is to appear later, he will present the physical chemical relationships which are of importance in the plant world, and show the real connection between the chemical and physical chemical facts and the biological results.

[1] Eloges historiques, Vol. 3, p. 156.

In this first volume he treats briefly, but clearly, the facts and relationships of such classes of compounds as alcohols, aldehydes, fats, waxes, carbohydrates, quinones, acids in ferns, glucosides, terpenes and complex compounds, resins, alkaloids, purines, polypeptides, proteids, dyestuffs, sulphur and phosphorus compounds, and the contents of the ashes obtained from plants.   S. F. ACREE.

THE BREWER'S ANALYST. By R. DOUGLASS BAILEY, F.C.S., F.R.M.S. New York: Van Nostrand & Co. pp. x + 423. Price, $5.

This work, though written primarily for those interested in the chemical problems associated with brewing, will find a use in a much wider field than might be imagined from the title, since it covers topics very extensively studied in both chemical and biological laboratories. It becomes a very useful compendium in any laboratory that deals with the analyses of the products of organic life. It is essentially a discussion of analytical methods, together with a consideration of their application and meaning. The scope of the work may be best understood by a brief review of the subjects treated.

A general consideration of analytical methods as applied to organic products is followed by a somewhat extended consideration of the use of the polariscope and its value in the study of sugars. A chapter on the carbohydrates will be of special value in biological or botanical laboratories, containing, as it does, comparative studies of starches from all the chief sources from which starch is obtained, together with photographs of the numerous types. The chemical nature and behavior of proteids, albuminoids, and enzymes cannot fail to be of great utility to all students who have to deal with these compounds in any chemical relations. The method of preparation of standard and other solutions gives in a condensed manner a type of information that every analyst is constantly desirous of using. An extended summary of the methods of analysis best adapted to the study of organic products occupies nearly one hundred and fifty pages, and contains a large amount of exactly the kind of information that is constantly wanted in any analytical laboratory. An extremely valuable chapter follows upon the interpretation of the results of analysts in determining purity or impurity of the materials examined, giving briefly the accepted conclusions that may be drawn from chemical analyses. While the first 325 pages are thus devoted almost wholly to chemical problems, they are followed by 150 pages which deal with microscopical and biological aspects of all problems related to brewing. Since bacteria, yeasts, and molds are all con-

cerned in brewing problems, this section of the work contains a valuable summary of the methods used in the study of these types of organisms, together with descriptions and figures of the important organisms associated with brewing in all its aspects. Finally, an appendix contains a long list of valuable tables.

For a laboratory dealing with the problems of brewing, this book, of course, has its special usefulness. But chemical, and especially biological laboratories will find much in it of great value. Its careful study of sugars and starches, its consideration of proteids and enzymes, its descriptions of yeasts and methods of their culture, and its valuable tables make it a very useful book of reference for any laboratory or any person dealing in a practical way with the chemical products of the living organism. H. W. Conn.

QUANTITATIVE ANALYSE DURCH ELEKTROLYSE. Von ALEXANDER CLASSEN. Fünfte Auflage in durchaus neuer Bearbeitung. Unter mitwirkung von H. CLOEREN. Mit 54 Textabbildungen und 2 Tafeln. Berlin: Verlag von Julius Springer. 1908. pp. XI + 336. Price, M. 10.

As is well known, this book, in its present form, is the outgrowth of the author's "Introduction to Quantitative Analysis by Electrolysis," published in 1882. This book has grown with each new edition, as more and better methods have been brought to light. The author tells us that the applications of quantitative electrical methods to both scientific and technical problems have increased so greatly in the last ten years that the present edition can be regarded as an essentially new work.

In studying and applying the various methods discussed in this book, Americans should not forget the splendid work in this field of Edgar F. Smith, which may not always be given the full credit that it deserves.

The application of electricity to quantitative analysis has revolutionized certain phases of this fundamental subject. It has been a comparatively short time since there were only a few metals that could be separated electrolytically. Now the number of such separations that can be effected is so large that metals which cannot thus be separated are the exception rather than the rule. A glance through the "Table of Contents" of this book will verify the above statement.

The work in hand comes from one of the leading authorities in the field, and is, therefore, indispensable to all analysts, whether they are dealing with technical or with scientific problems. H. C. J.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS. With Explanatory Notes and Stoichiometrical Problems. By HENRY P. TALBOT, PH.D., Professor of Inorganic and Analytical Chemistry in the Massachusetts Institute of Technology. Fifth edition, rewritten and revised. New York: The Macmillan Co.; London: The Macmillan Co., Ltd. 1908. pp. VII + 176. Price, $1.50.

This edition of Professor Talbot's well-known book has been entirely reset and revised so as to bring it up to date, but in general appearance and contents it differs but slightly from previous editions. As stated by the author in the preface, the book "has been prepared to meet the needs of students who are just entering upon the subject (of quantitative analysis) after a course of qualitative analysis. It is primarily intended to enable the student to work successfully and intelligently, without the necessity for a larger measure of personal assistance and supervision than can reasonably be given to each member of a large class." To this end the directions are given in great detail and are followed by notes explaining the reasons for each step. In the present edition, the ionic changes involved in the analytical procedure under discussion, the bearing of the mass law, etc., have been incorporated in these notes, while a brief discussion of the theory of electrolytic dissociation is retained in the appendix. Under the head of gravimetric analysis are given the determinations of chlorine in sodium chloride, of iron and sulphur in ferrous ammonium sulphate, of phosphoric anhydride in apatite, of lead, copper, and zinc in brass, of silica in silicates, and a complete analysis of limestone; under volumetric analysis are found the determinations of the alkaline strength of soda ash, of iron by the permanganate and bichromate processes, of antimony by means of iodine solution, of available chlorine in bleaching powder by titration with sodium arsenite solution, and of silver by the thiocyanate process. A distinctive feature of Professor Talbot's book is the space devoted to the discussion and presentation of stoichiometrical problems daily met with by the analyst and the solution of which often presents so much difficulty to the beginner until he has thoroughly mastered the underlying principles. The directions throughout are clear and the student is warned at every step against the possible sources of error. The book is undoubtedly one of the best of the many manuals of elementary quantitative analysis which we have.   C. A. R.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Band II., Heft 3. Dritte, vermehrte und verbesserte Auflage. Von PROF. DR. B. NEUMANN. Braunschweig: Vieweg und Sohn. pp. 659–1048. Price, M. 10.

This part deals with the analysis of fertilizers, soils, air,

ethereal oils, leather and tanning materials, glue, tobacco, rubber, gutta percha, and explosives, more than one-third of the volume being devoted to the latter subject.

The presentation of the various topics is admittedly considerably shorter than that in the book of a similar title edited by Lunge, there being usually no alternative method given; the one given may not always be the best, as it probably is not in the case of the determination of ozone in the air and fat in glue. The treatment of some subjects is not strictly in accord with current American practice, as would naturally be expected; the methods employed for the investigation of the other subjects, particularly tobacco, will be found useful.

For those desiring a concise manual of the analysis of these subjects the book would seem to be well adapted.   A. H. GILL.

SYNTHETIC INORGANIC CHEMISTRY. A Laboratory Course for First Year College Students. By ARTHUR A. BLANCHARD, PH.D., Assistant Professor of Inorganic Chemistry at the Massachusetts Institute of Technology. New York: John Wiley & Sons. pp. VIII + 89. Price, $1.

This is a collection of simple preparations of metals and of metallic salts. It is new in the introduction of questions and exercises, and in the application of the electrolytic dissociation theory and the mass law. The methods themselves are familiar.

The author argues in the preface for the value of such work following the laboratory study of the nonmetals and preceding qualitative analysis, as a means of familiarizing the student with the properties of the metals. He is using the method in his laboratory with good results.

It should be remembered that the great German laboratory teachers of the past—such as Wöhler, Liebig, and Bunsen—required inorganic preparation work. With the general rush to the field of organic chemistry instructors burdened with the daily task of instructing beginners in inorganic chemistry found relief from their burden by dropping all experimental work except analysis, giving the student a laboratory manual and plenty of analyses and leaving him alone.

Many manuals of inorganic preparations have appeared during the last twenty years in Germany and in this country, indicating a general discontent with the method of depending on analysis alone for laboratory practice. No one who has ever seen the eager interest of young students making preparations can doubt the pedagogic value of such work. The questions and exercises in Professor Blanchard's book enhance this value.   E. R.

THE DESIGN AND EQUIPMENT OF SMALL CHEMICAL LABORATORIES. By RICHARD K. MEADE, B.S., Editor of "The Chemical Engineer," Author of "Portland Cement" and "The Chemist's Pocket Manual," Chemist, Dexter Portland Cement Co., etc. Chicago: The Chemical Engineer Publishing Co. 1908. pp. III + 136. Price, $2.

This book is designed primarily to be of assistance to young chemists who find themselves confronted with the problem of designing and equipping a laboratory under conditions which may be entirely different from any under which they have before worked. Part of the book appeared in a series of articles in the *Chemical Engineer* during 1905. The fourteen chapters take up General Features, Hoods, Sinks and Water Supply, Desks, Table and Apparatus for Rapid Filtration, Ignition Table and Apparatus for Ignitions, Balance Support, Balance and Accessories, Heating Appliances, Preparation of Distilled Water, Apparatus for Electrochemical Analysis, Sampling Appliances, Assay Furnaces and Accessories, Miscellaneous Laboratory Equipment. The book is copiously illustrated with sample plans of laboratories, cuts of apparatus and laboratory devices, etc. In general, the names of the manufacturers of the various forms of apparatus described are given.   C. A. R.

AMERICAN

CHEMICAL JOURNAL

ON THE MOLECULAR CONDITION OF SALTS DIS-SOLVED IN A FUSED SALT. II. THE ELEC-TRICAL CONDUCTIVITY OF SALTS IN FUSED MERCURIC CHLORIDE.

By H. W. Foote and N. A. Martin.

In a previous article[1] it has been shown that a salt dissolved in a fused salt may be largely dissociated although its molecular weight, as shown by the freezing point method, is normal, provided the salt which acts as solvent is also largely dissociated. Thus, sodium chloride dissolved in sodium chlorate exhibits a normal molecular weight by the freezing point method, but if the chlorate is largely dissociated, as is indicated by its high conductivity, then sodium chloride may also be dissociated since its sodium ions would repress the dissociation of the chlorate and the effect, on the freezing point, of the two ions added would be the same as that of a single molecule.

The case is different, however, if the solvent salt is a non-conductor and therefore undissociated. In that case, if a salt such as sodium chloride were dissolved and dissociated,

[1] Foote and Levy: This Journal, **37**, 494.

its ions could not repress the dissociation of the solvent and the lowering in the freezing point, if the salt were completely dissociated, would be twice as great as the lowering if there were no dissociation. In other words, if a salt dissolves in a nonconducting fused solvent and exhibits a high conductivity, molecular weight determinations would be expected to give values much lower than the calculated ones. The case is similar to that of a salt dissolved in water.

Recently the molecular weights of the alkali chlorides and of mercurous and cuprous chlorides in fused mercuric chloride have been determined by Beckmann by means of the depression of the freezing point.[1] The molecular weights found agree very closely indeed with those calculated in every case except that of cuprous chloride, in which the values found lie between the values for CuCl and Cu_2Cl_2. The molecular weight of mercurous chloride corresponded closely to Hg_2Cl_2.

We found in preliminary experiments that fused mercuric chloride is a very poor conductor of the current but that the conductivity is very largely increased by the addition of a small amount of an alkali chloride. The case seemed interesting enough to warrant investigation and we have carried out a considerable number of conductivity determinations and shall attempt an explanation of the results.

The electrodes used in determining the conductivity are shown in Fig. I. The electrode at the left was fastened firmly by a screw in the cover, which was made of brass. The other electrode was passed through an opening in the cover, and was bent as represented and fastened securely in a porcelain tube to insulate it from the other electrode. The porcelain tube was held in the cover by a screw as shown. The ring in the cover was used in lifting the electrodes. We had some difficulty at first in fastening the electrode wire firmly in the porcelain tube. We succeeded best by roughening the platinum wire, then igniting it in the tube with a strong solution of water glass. Quartz tubes covered part of the wires as shown in the diagram. At first we used a lead glass coating which was fused on, but this was unsatisfactory. It appar-

[1] Z. anorg. Chem., **55**, 175.

ently conducted the current at a high temperature. The electrodes were made entirely of platinum and the wire was heavy enough so that it did not bend. The capacity of the vessel was determined in the ordinary manner with a standard potassium chloride solution.
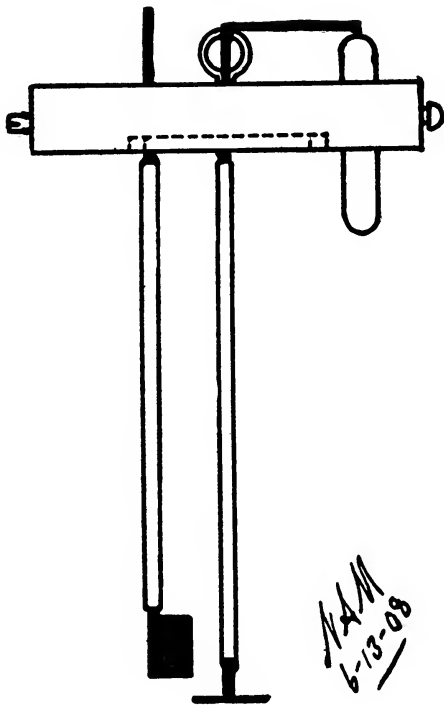
Fig. I.

The conductivity measurements were made by the customary Kohlrausch method at 282°. Several kilograms of a fusible mixture containing about equal parts of potassium

and sodium nitrates and sodium nitrite were used as a bath to keep the salts in the conductivity vessel fused at a constant temperature. The temperature of the bath varied by about one degree during the measurements.

The melting and boiling points of mercuric chloride lie very near together so that when fused, the salt volatilized rapidly, and in a series of determinations a correction in the amount of mercuric chloride had to be applied on account of loss by volatilization. The loss proceeded at a nearly uniform rate and an empirical correction was made. The density of fused mercuric chloride was found to be 4.36 at 282° and the volume of all solutions was calculated from the weight of mercuric chloride and this value for the density.

The specific conductivity of the ordinary C. P. mercuric chloride was found in one determination to be 2.5×10^{-4}. After recrystallizing, it became in one case 5.8×10^{-5}. All the recrystallized samples had a specific conductivity of the same order. All measurements were made with mercuric chloride which had been recrystallized one or more times. The specific conductivity of the mercuric chloride used in each case was deducted from the specific conductivity of the solution in order to calculate the molecular conductivities.

As the solutions could not conveniently be prepared at any particular concentration, the results calculated from two series of determinations were plotted and the conductivities at the dilutions shown in the table were read directly from the curves. The results were as follows:

Molecular Conductivity of Alkali Chlorides and Cuprous Chloride in Fused Mercuric Chloride at 282°.

V (liters).	CsCl.	KCl.	NH$_4$Cl.	NaCl.	CuCl.
2	. . . .	81.0	. . . .	61.5	70.0
4	. . . .	66.5	70.0	47.0	46.0
5	70.0	62.0	64.5	43.0	42.0
8	60.5	54.0	55.2	34.0	34.0
10	57.0	50.5	52.0	31.3	31.2
15	51.0	45.7	46.5	28.0	26.0
20	48.5	43.4	. . . .	. . . .	24.0
25	46.5	40.8	. . . .	. . . .	. . . .
30	44.0	38.5	. . . .	. . . .	. . . .

The curves representing the results graphically for the alkali chlorides are shown in Fig. II. Some of them have been prolonged slightly beyond the points actually determined. It will be noticed that the curves are all similar in type and that conductivity decreases with dilution in every case.
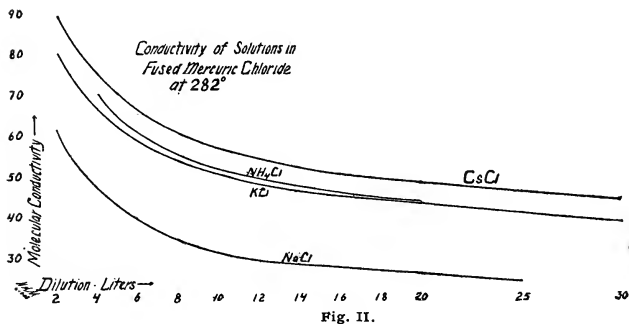
Fig. II.

The facts to be explained are that the chlorides have normal molecular weights as shown by the depression of the freezing point and that they have high molecular conductivity. The most probable explanation seems to be the formation of a complex salt which dissociates in solution:

$$2MCl + HgCl_2 \longrightarrow M_2HgCl_4 \longrightarrow \overset{+}{M} + \overset{-}{M}HgCl_4.$$
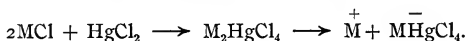
On this assumption, two molecules of alkali chloride give two ions, so that the depression due to the ions would be the same as that due to the original salt. The formation of a compound, $MHgCl_3$, appears to be impossible. This salt would form two ions from one molecule of alkali chloride, so in this case the molecular weight would necessarily be lower than the calculated.

Some indirect evidence bearing on the probable formation of the salt M_2HgCl_4 was obtained. A corresponding salt of a bivalent element, $MHgCl_4$, could not dissociate in the same manner. We attempted to prepare solutions containing the

chlorides of bivalent elements in order to measure their conductivity and were surprised to find they were nearly all insoluble. Thus barium chloride was insoluble although the presence of mercuric chloride increases its solubility in water enormously. The only chloride of a bivalent element which we found to be soluble was cupric chloride, which was slightly soluble, giving a distinct brown color to the solution. The conductivity of mercuric chloride was not, however, perceptibly changed by the presence of the cupric chloride. Anhydrous ferric chloride and mercurous chloride are also soluble in mercuric chloride but their solutions, too, are nonconductors. The readiness with which the alkali chlorides dissolve, on the other hand, is very striking. It appears then that alkali chlorides which can dissociate according to the equation $M_2HgCl_4 \longrightarrow M + MHgCl_4$ are very readily soluble while if the salt is of such a type that it cannot dissociate in this way, it either does not dissolve or else, if dissolved, it does not conduct the current.

If the complex M_2HgCl_4 is formed, it must be practically all dissociated, for if it were not, two molecules of alkali chloride would yield one molecule of complex salt, and molecular weight determinations would give high results.

The dissociation according to the expression

$$2NaCl + HgCl_2 \longrightarrow \overset{+}{Na} + Na\overset{-}{HgCl_4}$$
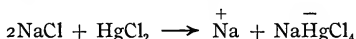
is independent of the dilution, as the number of ions is equal to the number of molecules of sodium chloride. The molecular conductivity in this case should not change with the concentration. The results, however, show gradual increase of conductivity with the concentration until the more concentrated solutions are reached, when the conductivity rises rapidly. This is very likely due to the formation of increasing amounts of some other complex salt in solution, the amount being small at first but increasing in the more concentrated solutions. Thus the salt M_3HgCl_5 may be formed, dissociating into $\overset{+}{M} + \overset{+}{M} + \overset{=}{MCl_5}$. This would not affect the molecular weight but would change the conductivity.

Whether all the dissolved alkali chloride is converted into a complex salt or not we have no certain means of determining, but the fact that nearly all salts of a diacid base, like barium, are insoluble, while the alkalies are exceedingly soluble, makes it very probable that the solubility is due to the formation of the dissociated complex salt and that the action is nearly or quite complete.

The difference in the behavior of cuprous and mercurous chlorides is noticeable, solutions of mercurous chloride not being conductors while solutions of cuprous chloride conduct readily. Beckmann found the molecular weight of mercurous chloride corresponded to Hg_2Cl_2 and that of cuprous chloride to a mixture of $CuCl$ and Cu_2Cl_2. Apparently the double molecules do not form dissociated complex molecules with the solvent while the single molecules of cuprous chloride behave like sodium chloride, forming the dissociated double salt.

New Haven, Conn.,
    April, 1909.

STUDIES IN CATALYSIS:

ON THE FORMATION OF ESTERS FROM AMIDES AND ALCOHOLS.

[TENTH COMMUNICATION ON CATALYSIS.]

By S. F. Acree.

Esters, amides, cane sugar, oximes, etc., are hydrolyzed far more rapidly in aqueous solutions when in the presence of strong mineral acids than when such acids are absent, and this catalysis is now generally explained on the assumption of the formation of intermediate compounds by the union of the acid catalyzer and the ester, sugar, etc.

Kastle,[1] Euler,[2] Acree,[3] Bredig,[4] Lapworth,[5] Stieglitz,[6] and Goldschmidt[7] have all contributed researches which, as a whole, showed that the ideas involved in using the theory of ionization in acid catalysis, together with the assumption of intermediate salts or double compounds, are most probably the correct ones when it is postulated that the cation of the ester salt is hydrolyzed. In 1904–'05 Acree and Brunel[8] proposed the theory and began experimental work to prove that in the *alkaline catalysis* of the formation of esters from acids and alkyl halides the *anion* of the salt is the substance transfromed, and Acree and Johnson predicted the same of the hdyrolysis of esters and amides. The close analogy of the theory of acid catalysis to Acree's theory of alkaline[9] catalysis can be seen at a glance from the following table:

[1] See P. Am. Assn. Adv. Sci., **47**, 238, for an abstract of the original article, which was never published in full, and which Prof. Kastle kindly sent me at my request.

[2] Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356; Z. physiol. Chem., **52**, 146.

[3] Acree and Hinkins: THIS JOURNAL, **28**, 370. This work was entirely completed in the spring of 1901. I believe that the mechanism of the reactions assumed in this paper is wrong and have adopted the view first presented by Kastle and Bredig. See R. F. Brunel's dissertation, Johns Hopkins, 1906, begun in 1904–5; J. Am. Chem. Soc., **30**, 1755; THIS JOURNAL, **37**, 71, 410; **38**, 258, 489, 746; **39**, 145, 226, 300; and especially, **38**, 342, 343, for my views on the mechanism of reactions. Euler has changed his views on the mechanism of catalytic reactions (Z. physiol. Chem., **52**, 146).

[4] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528; Ergebnisse der Physiologie, Vol. I., p. 134 (1903); Biochem. Z., **6**, 283; Ber. d. chem. Ges., **41**, 740, 752; and many other articles.

[5] Mellor's Statics and Dynamics, p. 289. See especially J. Chem. Soc., **93**, 30, 85; Chem. News, **97**, 248, 309.

[6] Congress of Arts and Sciences, St. Louis, 1904, **4**, 276; THIS JOURNAL, **31**, 458; **39**, 29, 166, 402, 437, 586, 719.

[7] Ber. d. chem. Ges., **29**, 1369, 1899; **32**, 3390; **39**, 97, 109, 711; Z. physik. Chem., **56**, 1, 385; and many other papers.

[8] Brunel's Dissertation, Johns Hopkins University, 1906.

[9] For a fuller mathematical discussion of the theory of the formation and decomposition of the complex cations and anions see THIS JOURNAL, **37**, 71, 410; **38**, 258, 489; **39**, 124; Ber. d. chem. Ges., **41**, 3199. Dr. Reid now has evidence that the catalysis of amides by alkalies may not be exactly like saponification.

$$CH_3CONH_2 + H_2O \longrightarrow CH_3CON\overset{+}{H_3} + \overset{-}{OH}$$
Weak base — few cations

$$CH_3CONH_2 + H_2O \longrightarrow CH_3CON\overset{+}{H_3} + \overset{-}{OH} + H_2O \longrightarrow CH_3C(OH)_2\overset{+}{NH_3} + \overset{-}{OH} \longrightarrow CH_3COOH + NH_4OH$$
few cations — slow reaction

$$CH_3CONH_2 + HCl \longrightarrow CH_3CON\overset{+}{H_3} + \overset{-}{Cl} + H_2O \longrightarrow CH_3C(OH)_2\overset{+}{NH_3} + \overset{-}{Cl} \longrightarrow CH_3COOH + NH_4Cl$$
many cations — many complex cations — fast reaction

$$UrH + C_2H_5I \longrightarrow \overset{-}{Ur} + \overset{+}{H} + C_2H_5I \longrightarrow \overset{-}{Ur.IC_2H_5} + \overset{+}{H} \longrightarrow \overset{-}{Ur.C_2H_5} + \overset{+}{H} + \overset{-}{I}$$
Weak acid — few anions — few complex anions — slow reaction

$$UrH + NaOH \longrightarrow \overset{-}{Ur} + \overset{+}{Na} + C_2H_5I \longrightarrow \overset{-}{Ur.IC_2H_5} + \overset{+}{Na} \longrightarrow \overset{-}{Ur.C_2H_5} + \overset{+}{Na} + \overset{-}{I}$$
many anions — many complex anions — fast reaction

$$CH_3COOR + \overset{+}{H} + \overset{-}{OH} \longrightarrow CH_3C(OH)(OR)(\overset{-}{O}) + \overset{+}{H} \longrightarrow CH_3COOH + ROH$$
Weak acid in water — few complex anions — slow reaction

$$CH_3COOR + H_2O + \overset{+}{Na} + \overset{-}{OH} \longrightarrow CH_3C(OH)(OR)(\overset{-}{O}) + \overset{+}{Na} \longrightarrow CH_3\overset{-}{COO} + \overset{+}{Na} + ROH$$
many complex anions — fast reaction

In 1907, Acree,[1] Johnson, and Nirdlinger furnished quantitative evidence that the hydrazide, amide, and oxime cations are hydrolyzed,

$$(CH_3)_2C = NOH + \overset{+}{H} + \overset{-}{Cl} + H_2O \rightleftarrows$$

$$(CH_3)_2C = \overset{+}{N}HOH + \overset{-}{Cl} + H_2O \rightleftarrows$$

$$(CH_3)_2C\overset{OH}{\underset{+}{\diagdown NH_2OH}} + \overset{-}{Cl} \rightleftarrows (CH_3)_2CO + \overset{+}{N}H_3OH + \overset{-}{Cl},$$
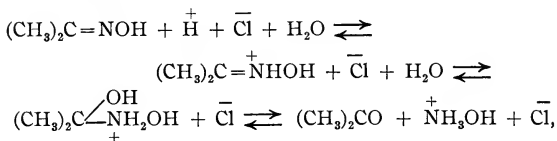
and in 1908 Stieglitz[1] and his coworkers published a number of brilliant researches on the imidoesters which had been under way since 1898. Pinner had shown more than 16 years before that the imidoester salt is hydrolyzed and Stieglitz proved conclusively that the imidoester cation is catalyzed.

In connection with the above theory of intermediate compounds it should be mentioned that Bredig[1] and his coworkers have studied the catalytic action of cyanide ions in benzoin formation, of hydrogen ions in the decomposition of diazoacetic ester, of iodide ions on the change of hydrogen peroxide, etc. Lapworth[1] studied the catalytic action of hydrogen ions on the bromination of ketones, on esterification and saponification, and on oxime formation. Goldschmidt[1] has investigated the catalytic action of acids on esterification, reduction and oxidation phenomena, etc., and Kastle[2] the catalytic action of enzymes on ester formation and decomposition, the action of acids in the bromination of phenols, formation of esters, etc. It is evident then that in the last decade a large number of workers have been studying catalysis from the same general point of view and the future bids fair to clear up a large number of the very important problems of this field. Catalysis is regarded as only a part of the broad domain of *the study of the mechanism of reactions*, all of which must be investigated from the same general point of view.

[1] *Loc. cit.*

[2] P. Am. Assn. Adv. Sci., **47**, 238; THIS JOURNAL, **24**, 491; **26**, 518; **29**, 397, 563; **31**, 521; **32**, 376.

ON THE REARRANGEMENT OF ACETYLHALOGENAMINOBENZENE
DERIVATIVES.

Acree and Johnson published a very full[1] account of all
the researches on catalysis which had appeared up to 1907,
and developed fully the correct equations for treating mathe-
matically the theory of intermediate compounds, this hav-
ing been done only incompletely by Bredig, Lapworth, Stieg-
litz, Goldschmidt, etc. These equations show that two of
the three old so-called laws of catalysis can not possibly
hold in all catalytic reactions, these laws being merely "ap-
proximate expressions of special reactions," such as the in-
version of cane sugar, reversible ester formation, and hy-
drolysis of amides. The second and third so-called laws of
catalysis, which postulated that "the catalyzer affects the
velocity constant directly in proportion to the concentration
of the catalyzer" and that "a change in the concentration
of the catalyzer does not change the equilibrium point in re-
versible reactions," were developed under the assumption
that the catalyzer does not take part in the reaction. But
from the newer point of view we look upon a catalyzer as a
substance which accelerates (or suppresses)[2] a reaction chem-
ically because it forms an intermediate addition product
which is more (or less) reactive than the original noncatalyzed
reacting substances. From this point of view there is no
sharp dividing line between the old so-called cases of pure
catalysis, such as the hydrolysis of cane sugar, esters, etc.,
in which the amount of salt formed is very small, and those
cases in which the amount of salt or double compound pres-
ent is very large and which cannot be called catalysis at all
in the old sense. On this assumption it was developed math-
ematically that there are many conditions under which these
two laws can hold, and others under which they cannot hold,
whether there are only traces or much of the intermediate

[1] Bredig and also Lapworth have referred to this article as a general summary
of the facts of importance to catalysis (Ber. d. chem. Ges., **41**, 754, 755; J. Chem. Soc.,
93, 2163).

[2] This does not necessarily include the catalytic effect of solvents in changing
eaction velocities because of change in viscosity, vapor tension, heat of dilution, and
unknown factors which influence reactions.

compound formed. For instance, it was shown experiment-
ally by Blanksma[1] and more fully by Acree and Johnson[2]
that hydrochloric acid causes a catalysis of acetylbrom(chlor)-
aminobenzene into *p*-brom(chlor)acetanilide in proportion
to the square of the concentration of the hydrochloric acid
instead of the first power of this concentration as demanded by
the above second law of catalysis. The simplest[3] explana-
tion of this is that the acetylbrom(chlor) aminobenzene unites
not only with the hydrogen ion but also with the chloride
ion, present in the same concentration, which therefore
acts as a *cocatalyzer*[4] with the hydrogen ion. This view is
supported by a large number of other facts, such as the fol-
lowing: the reaction velocity of acetylchloraminobenzene
in acetic acid, or in a mixture of acetic acid and hydrochloric
acid, is increased by the addition of potassium chloride (and
hence chloride ions) because the increase in the concentra-

[1] Rec. trav. chim., **21**, 366; **22**, 290.

[2] THIS JOURNAL, **37**, 410; **38**, 265.

[3] Some other explanations, based partly on other mechanisms of the action of
the hydrogen or halide ion as a cocatalyzer, have suggested themselves. These will
be treated experimentally but do not seem probable at present. The cation may be
also undergoing transformation with a much smaller velocity. The explanation
proposed by Cohen and Cross (P. Chem. Soc., **23**, 148; THIS JOURNAL, **39**, 431) is cer-
tainly not complete (see *loc. cit.* and THIS JOURNAL, **38**, 746; **39**, 544).

[4] The bromide, acetate, sulphate, etc., ions can be used instead of the chloride
ions as a cocatalyzer in this reaction: *i. e.*, acetylbromaminobenzene is changed into
p-bromacetanilide by various acids. But in this reaction the bromide ion is at least
1000 times as active as the chloride ion as a cocatalyzer, and acetate and sulphate
ions are far less active than the chloride ion. Likewise acetylchloraminobenzene is
changed into *p*-chloracetanilide by hydrochloric acid very smoothly at 4°, while hydro-
bromic acid causes a corresponding change of this chloramide derivative into the *p*-
bromacetanilide at 3° at least 100 times as rapidly. These facts therefore give further
light on the possible action of co-enzymes because the mechanism of our reaction is
clear and recalls certain very interesting co-enzyme reactions. Pepsin seems to be
practically inactive unless hydrogen ions are present, and trypsin does not react in
the absence of hydroxyl ions. Asparagine seems to act as a specific co-enzyme with
amylase, and zymase seems to have two enzymes which act together, either alone be-
ing inactive (See Bayliss: "The Nature of Enzyme Action," p. 65). The reactions of
these substances, as well as those of the anti-toxins, may all depend entirely upon the
velocity of formation and change of the intermediate *catalyzer.cocatalyzer.substrate*
double compounds. But we must distinguish in all cases between the laws for true
solutions and those for colloidal solutions or suspensions, a fact too often overlooked.
The fact that these two cocatalyzers, the bromide ion and the chloride ion, are about
as closely related chemically as any substances that we have, and yet have such greatly
different catalytic effects in the above reactions, may be of great importance in a
large number of phenomena of biological chemistry; two apparently related substances,
ions or enzymes, may sometimes have widely different actions in the plant and animal
world.

tion of the chloride ions causes an increase in the concentration of the undissociated salt, as demanded by the equations below. The concentration of this undissociated acetylbrom-(chlor)aminobenzene salt, which is the substance undergoing transformation, is roughly proportional to the square of the concentration of the hydrochloric acid when the acid is nearly completely ionized.

$$\text{I.} \quad CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows$$
$$CH_3CONHCl_2C_6H_5 \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}.$$

$$\text{II.} \left\{ \begin{matrix} CH_3CONBrC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \\ CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Br} \end{matrix} \right\} \rightleftarrows \underset{\text{trace}}{CH_3CONHClBrC_6H_5} \longrightarrow$$
$$CH_3CONH_2ClC_6H_4Br \longrightarrow CH_3CONHC_6H_4Br + \overset{+}{H} + \overset{-}{Cl}.$$
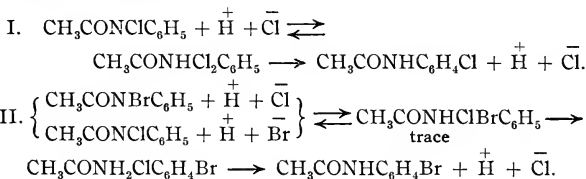
Now the data of Blanksma, and those of Acree and Johnson obtained in the preliminary study of the catalytic action of hydrochloric acid on acetylchloraminobenzene, show roughly that this formulation is probably correct. The uncertainty in the calculations for the rather concentrated solutions necessary for the study of the reaction, together with the large analytical error, make exact calculations of no value. The data obtained show roughly, however, that the reaction velocity is proportional to the *square* of the concentration of the hydrochloric acid, which is represented in terms of $M = 10$ cc. of 28.67 per cent hydrochloric acid in 500 cc. of 30 per cent acetic acid solution. The values for K are those obtained in 30 per cent acetic acid solution.

K.	$0.5 M$.	M.	$1.5 M$.	$2 M$.	$2.5 M$.	$3 M$.	$5 M$.
Found	0.00103	0.0036	0.0087	0.0146	0.0239	0.0313	0.113
Calc.	0.00098	0.0039	0.0087	0.0154	0.0242	0.0348	0.097

In the study of the action of hydrobromic acid on acetylchloraminobenzene in 10 per cent acetic acid at $3°$, however, the reaction was found to proceed so rapidly in even dilute solutions of hydrobromic acid that much more exact data could be obtained. We have therefore now calculated the constants by making the proper corrections for the suppres-

sion of the ionization of the acetic acid by the hydrobromic and hydrochloric acids, taking $K = 0.000018$ at $3°$ and considering the ionization of the hydrobromic and hydrochloric acids to be the same in the acetic acid solution as it is in water, both of which assumptions are not far from right.

The application of the mass law to reactions II. above gives us the approximate equation,

$$\frac{dx}{dt} = K(C_a - x)(C_{Br} - x)C_H \text{ or } KC_HC_{Br} = \frac{x}{t(A-x)},$$

in which the proper concentrations, in gram molecules per liter, of hydrogen ions, C_H, bromide ions, C_{Br}, and acetyl-chloraminobenzene, C_a, must be substituted. When this is done the following rounded values are obtained:

Table.	C_a.	C_{HBr}.	C_{Br}.	C_H.	$KC_{Br}C_H$.	K.
I.	0.0024	0.0024	0.00232	0.00676	0.0111	710
II.	0.0040	0.0040	0.00390	0.00770	0.0210	700
III.	0.00586	0.00586	0.00565	0.0090	0.0388	760
IV.	0.0078	0.0078	0.00746	0.01033	0.0568	740
V.	0.01134	0.01134	0.01070	0.0130	0.1000	720
VI.	0.01714	0.01714	0.01595	0.0176	0.2050	730
VII.	0.0210	0.0210	0.0194	0.0244	0.345	730

Average. 730

The values for K give what we must call a very good constant when we consider the difficult experimental conditions, especially the fact that light affects the reaction velocity so greatly. We are justified then in making a further study of this problem from this point of view.

Another problem which we developed theoretically and proved experimentally was that the third law of catalysis cannot hold in some cases, whether the concentration of the intermediate compound be large or small, and yet may hold approximately in other reactions. To illustrate with one of many possible examples, it was seen that if in a reversible reaction we have a base in each of the opposing sets of reacting substances, and if the reaction is catalyzed

by acids because of the formation of more reactive salts of the bases, then the equilibrium point of the reaction must be altered by a change in the amount of acid added if the two bases have not the same affinity constants. We chose the reversible formation of oximes to test this principle, and Johnson's experimental work, and also that of Lapworth[1] and his coworkers, proved beyond question that our ideas are correct.

$$(CH_3)_2CO + NH_2OH \rightleftharpoons (CH_3)_2C = NOH + H_2O.$$

$$(CH_3)_2CO + \overset{+}{N}H_3OH + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2C(OH)\overset{+}{N}H_2OH + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2C = \overset{+}{N}HOH + H_2O + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2C = NOH + \overset{+}{H} + \overset{-}{Cl} + H_2O,$$

or

$$(CH_3)_2CO + NH_2OH + \overset{+}{H} + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2CO.\overset{+}{H} + NH_2OH + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2C(OH)\overset{+}{N}H_2OH + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2C = \overset{+}{N}HOH + H_2O + \overset{-}{Cl} \rightleftharpoons$$
$$(CH_3)_2C = NOH + \overset{+}{H} + \overset{-}{Cl} + H_2O.$$
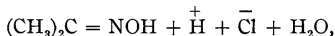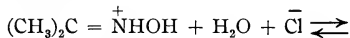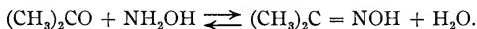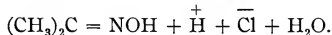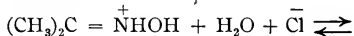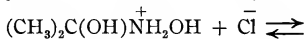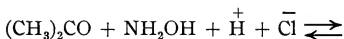
Of course, the same line of reasoning can be extended to include the formation of many other intermediate compounds by the action of alkalies, salts, enzymes, organic substances, etc. Professor Bredig has kindly called my attention to the fact that he too has pointed out in the *Ergebnisse der Physiologie*,[2] before our article appeared, that the second and third laws do not always hold. Abel,[3] Euler,[4] and Stieglitz[5] have all recently discussed the same question, and in view of Acree and Johnson's mathematical and experimental proof these

[1] J. Chem. Soc., **91**, 1133.
[2] Vol. I., p. 134.
[3] Z. Elek. Chem., **13**, 555.
[4] Z. physiol. Chem., **52**, 146.
[5] *Loc. cit.*

three old so-called laws of catalysis may be said to be abandoned as a rigid basis for work.

Especially was it developed by Acree and Johnson that reactions may be the result of several independent simultaneous or side reactions, involving both the dissociated and undissociated salts, the free bases or acids, etc., and this point of view should guide all quantitative work. It was shown clearly by our work, and that of Lapworth, on the oximes that at least two and perhaps three reactions may, under certain conditions, be taking place side by side. Mr. Desha is continuing the work on the oximes. We wish our colleagues to leave to us for some time the study of the formation of the amidoximes from the hydroxylamines and amidine salts, and of the hydroxamic acid derivatives. The study of the formation, hydrolysis, and other reactions of these substances should throw important light on the theory of catalytic processes.

ON THE HYDROLYSIS AND ESTERIFICATION OF AMIDES.

Acree and Nirdlinger[1] showed experimentally in a preliminary study that the hydrolysis of amides may be explained on the assumption of the hydrolysis of amide cations,

$$CH_3CONH_2 + \overset{+}{H} + \overset{-}{Cl} + H_2O \longrightarrow$$
$$CH_3CO\overset{+}{N}H_3 + \overset{-}{Cl} + H_2O \longrightarrow CH_3COOH + N\overset{+}{H}_4 + \overset{-}{Cl},$$
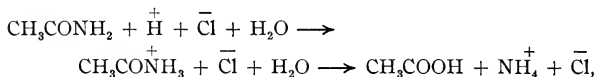
and it was pointed out that the work of Ostwald,[2] Remsen and Reid,[3] and Crocker,[4] which was undertaken from quite another aspect, harmonized with our point of view. I have had the good fortune now, through the aid of a grant from the Carnegie Institute of Washington, to have this work taken up again by Dr. E. E. Reid to extend his own former work and to give light on our theory. He is studying the hydrolysis and alcoholysis of amides by acids and alkalies, as he reports in the succeeding article.

[1] This Journal, **38**, 489.
[2] J. prakt. Chem., **135**, 1.
[3] This Journal, **21**, 281; Reid: *Ibid.*, **24**, 397.
[4] J. Chem. Soc., **91**, 593.

I predicted that amides, anilides, hydrazides, etc., would yield esters in alcoholic hydrochloric acid, according to one or both of the following reactions,[1] more probably the first one:

$$CH_3CONH_2 + \overset{+}{H} + \overset{-}{Cl} \longrightarrow CH_3C\overset{+}{O}NH_3 + \overset{-}{Cl} + ROH \quad \Big\} \longrightarrow$$
$$CH_3CONH_2 + \overset{+}{H} + \overset{-}{Cl} \longrightarrow CH_3CONH_2 + \overset{-}{Cl} + ROH.\overset{+}{H} \quad \Big\}$$
$$CH_3C(OH)(OR)\overset{+}{N}H_3 + \overset{-}{Cl} \longrightarrow CH_3COOR + \overset{+}{N}H_4 + \overset{-}{Cl}.$$
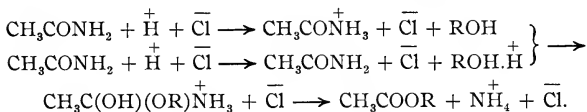
Dr. Reid also saw this problem independently and has since found that amides give practically quantitative yields of esters. Messrs. Bransky and Chazal have also found that benzphenylhydrazide and benzanilide give excellent yields of ethyl benzoate. The study of the esterification of amides, anilides, hydrazides, etc., is of especial interest from several points of view. The reactions are exactly analogous, on the one hand, to those of the hydrolysis of esters and amides, and, on the other hand, to those of the esterification of organic acids, which have been the subject of detailed study in recent years by Goldschmidt[2] especially, and by Lapworth,[3] Weg-

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[1] Although the formation of an imidoester by the alternate reaction,

$$CH_3C(OH)(OR)\overset{+}{N}H_2 \longrightarrow CH_3C(OR) = \overset{+}{N}H_2 + H_2O,$$
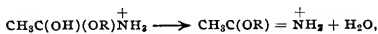
and the formation of an ester or ortho-ester from the imidoester salt,

$$CH_3C(OR) = \overset{+}{N}H_2 + H_2O \longrightarrow CH_3COOR + \overset{+}{N}H_4$$
$$CH_3C(OR) = \overset{+}{N}H_2 + 2ROH \longrightarrow CH_3C(OR)_3 + \overset{+}{N}H_4,$$
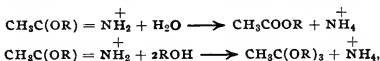
have never been observed, and the constants of the reactions indicate that these cannot be present in large quantity, yet this may be found to be true in other cases in later studies. Dr. Reid has found that the *m*-nitrobenzamide gives a quantitative yield of the ethyl *m*-nitrobenzoate. There seems to be a general tendency in acid and alkaline catalysis for the catalyzed substance, itself an acid or base, to go over into the salt of a stronger acid or base when the reaction goes nearly or quite to completion. Acree and Johnson found, however, that in reversible oxime formation the stronger base, hydroxylamine, goes partly into a weaker base, acetoxime. It is easy to show that *in all cases* the reactions take place because of a decrease in the free energy of the system as demanded by the second law of thermodynamics. This point of view has been insisted upon and used most brilliantly for years by Michael, for the organic chemists, and by Euler, Plank, Nernst, Abegg, and many other physical chemists. A brilliant field for investigation in organic chemistry is the study of changes in free and total energy of reacting systems by the use of electromotive force measurements, calorimetric data of many kinds, etc. We propose to study the reactions of hydroxylamines, alcohols anilines, semicarbazides, etc., with the salts of amides and other similar compounds.

[2] Ber. d. chem. Ges., **39**, 711; Z. physik. Chem., **60**, 728.

[3] *Loc. cit.* and also J. Chem. Soc., **93**, 2163, 2187; P. Chem. Soc., **24**, 101, 152.

scheider[1] and Kailan, Julius Meyer,[2] Rosanoff,[3] Michael,[4] etc. New evidence obtained by work on the amides should throw light on the entire subject of catalysis. There is, further-more, a great advantage in working with these nitrogen com-pounds in that they are stronger bases than the organic es-ters or acids and hence the concentration of the salt[5] formed can be measured more easily, although the amount of this salt is so small that these reactions might still be looked upon as belonging to the old field of so-called pure catalysis. An-other great advantage can be seen from the following: In studying the rates of formation of esters from organic acids and alcohols, Goldschmidt especially, and also Bredig and Fraenkel,[6] Kailan,[7] and Gyr[8] recently, have observed that even small amounts of water affect the reaction velocity very greatly, and render interpretations of the reactions un-certain. It is absolutely impossible to eliminate this dis-turbing factor in the esterification work because water is formed in the reaction:

$$CH_3COOH + ROH \rightleftarrows CH_3COOR + H_2O.$$
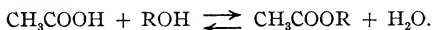
But no appreciable amount of water is formed in the esteri-fication of amides and hence a very great disturbing factor is eliminated. The absence of this factor not only shows itself in the concordance of Dr. Reid's velocity constants, but also renders possible much more accurate work in the determination of the conductivities, concentrations, or hy-drolysis, of the reacting salts, and of change in viscosity, vapor tension, heat of dilution, etc., of the solutions.

But a very great reason for studying the esterification of

[1] Sitzun. Wien., **116**, II., 55; Ber. d. chem. Ges., **39**, 1055; Ann. Chem. (Liebig), **351**, 186.

[2] Z. Elek. Chem., **13**, 186, 485, 494; Z. physiol Chem., **66**, 81.

[3] J. Am. Chem. Soc., **30**, 1895, 1908.

[4] Ber. d. chem. Ges., **42**, 310, 317.

[5] Acree and Johnson found that a number of organic esters and other carbonyl compounds lower the conductivity of alcoholic and aqueous hydrochloric acid a very slight amount, probably due to the formation of ester salts. Goldschmidt failed to detect any such salt formation by ethyl phenylacetate. Acree and Nirdlinger: This JOURNAL, **38**, 489.

[6] Biochem. Z., **6**, 308.

[7] *Loc. cit.*; Monatsh. Chem., **28**, 559, 571, etc.

[8] Ber. d. chem. Ges., **41**, 4322.

the amides was the desire to secure light on certain phases which have come out not only in our own work but also in Goldschmidt's theory of the formation of esters from organic acids and alcohols in the presence of strong acids. This brilliant worker in the field of quantitative organic chemistry has proposed, as an alternative to the generally accepted views, the theory that the hydrogen ions of a catalyzing acid unite with the alcohol and that this complex cation reacts with the organic acid as follows:

$$CH_3COOH + \overset{+}{H} + \overline{Cl} + ROH \rightleftarrows$$
$$CH_3COOH + ROH.\overset{+}{H} + \overline{Cl} \rightleftarrows$$
$$CH_3C(OH)(OR)(OH.\overset{+}{H}) + \overline{Cl} \rightleftarrows$$
$$CH_3COOR + H_2O.\overset{+}{H} + \overline{Cl} \rightleftarrows$$
$$CH_3COOR + H_2O + \overset{+}{H} + \overline{Cl}.$$
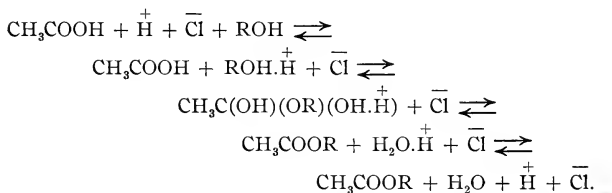
This theory is analogous to that proposed by A. A. Noyes several years ago to account for catalytic hydrolysis. Goldschmidt has without doubt gone more deeply into the study of esterification than other workers and his views are to be given great respect. Dr. Reid's work seems to me all the more important, therefore, because the study of the esterification of amides would throw light on some questions that cannot be taken up or solved in Goldschmidt's work.

For instance, Goldschmidt cannot easily measure accurately the real amount of the cation formed by the union of the hydrogen ion and the alcohol or organic acid to be esterified. In the work on the amides, however, Acree and Nirdlinger showed by conductivity methods that an amide salt is actually formed, and we shall attempt to measure the basic and acid constants of a large number of such substances as acetamide, benzamide, mono- and dimethylbenzamide, benzhydroxamic acid and its esters, aminoacetic acid and its homologues, the amides and especially half amides of dibasic acids, such as succinic acid, etc. This is a very important question, because if it were possible to measure accurately the real concentrations of the amide salt and of the alcoholated hy-

drogen ions it would obviously be possible to determine whether the decomposing complex cation[1] $CH_3C(OR)(OH)\overset{+}{N}H_3$ (or undissociated salt) is formed by the union of the alcohol and the amide salt or ion, or the union of the alcoholated hydrogen ion with the amide, or both. When the amide is a very weak base the hydrogen ions will divide themselves between the water, alcohol, and amide, but when the amide is a very strong base it will use practically all of the hydrogen ions for salt formation, and there will be no appreciable concentration of hydrated or alcoholated hydrogen ions remaining. Lapworth[2] and Goldschmidt[3] have recently treated this subject extensively mathematically and experimentally. Goldschmidt's theory requires that the addition of water shall lower the esterification constants of all organic acids to about the same extent, and this has been verified experimentally by him. But I predicted that the change in constant would vary with the amide, and Dr. Reid finds variations as large as 50 per cent; much work is needed from all these points of view.

To approach this problem it would obviously be necessary to know the concentrations of the salts as well as to measure the degree of alcoholation and hydration of the hydrogen ion by methods like those of Frazer and Holmes,[4] Noyes and Washburn,[5] and Buchböck.[6] This is entirely analogous to the problem involved in the study of the formation of esters from alkyl halides and salts, which Acree,[7] and later Goldschmidt,[8] supposed takes place through the formation and the decomposition of a complex anion, and which we are studying minutely in this laboratory.

$$C_2H_5I + \overset{+}{Ag} + \overset{-}{N}O_3 \rightleftarrows C_2H_5I.\overset{-}{N}O_3 + \overset{+}{Ag} \rightleftarrows$$
$$C_2H_5NO_3 + \overset{+}{Ag} + \overset{-}{I}.$$
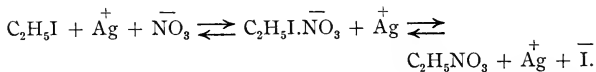
[1] This is given only as the most probable formula: there may be several forms of this salt in equilibrium. Acree and Johnson: This JOURNAL, **38**, 337, 341.

[2] J. Chem. Soc., **93**, 2187.

[3] Z. Elek. Chem., **15**, 4.

[4] This JOURNAL, **40**, 319.

[5] J. Am. Chem. Soc., **31**, 322.

[6] Z. physik. Chem., **55**, 563.

[7] This JOURNAL, **38**, 262; **39**, 244; Ber. d. chem. Ges., **41**, 3214.

[8] Z. Elek. Chem., **14**, 581.

Of course, both of the above reactions of the amides may be taking place side by side, a phase that we are investigating especially, as Lapworth and Acree, Johnson, and Desha have found such to be the case in oxime formation.

In this connection I wish to call attention to the light which Dr. Reid's work sheds on another important phase of this general problem. About seventeen years ago Pinner published in his book, *Die Imidoaether und ihre Derivate,* the results of investigations which showed that the hydrochlorides of imidoesters are not only hydrolyzed into ammonium chloride and the corresponding ester, but that they are also alcoholyzed or esterified into ammonium chloride and the corresponding ortho esters, these two reactions being therefore entirely analogous.

$$ROCH = NH_2Cl + H_2O \longrightarrow ROCHO + NH_4Cl$$
$$ROCH = NH_2Cl + 2ROH \longrightarrow ROCH(OR)_2 + NH_4Cl$$
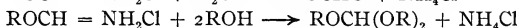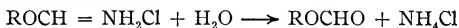
Claisen[1] has used this reaction for the preparation of nascent ortho esters in the presence of ketones in order to obtain ketals, and recently Reiter and Hess[2] have taken up this study again. Stieglitz[3] has proposed a theory to explain this reaction based on the assumption of the formation and reactions of an olefine compound, such as $CH = C(OC_2H_5)_2$. He states (note 3, page 721) that the "*difference* (italics mine) in the result of this action and that of water on such salts" suggested the following reactions:

$$CH_3C(= \overset{+}{N}H_2)OC_2H_5 + HOC_2H_5 \longrightarrow$$
$$CH_3C(\overset{+}{N}H_3)(OC_2H_5)_2 \longrightarrow CH_2 = C(OC_2H_5)_2 + \overset{+}{N}H_4$$
$$\text{and} \quad CH_2 = C(OC_2H_5)_2 + HOC_2H_5 \longrightarrow CH_3C(OC_2H_5)_3;$$
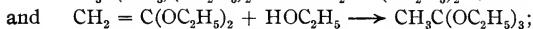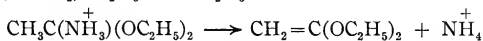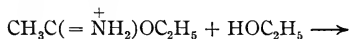
and he found further evidence for this point of view in the fact that in the case of cyanacetic ester an olefine compound, $ROOCCH = C(OC_2H_5)_2$, was actually obtained as an intermediate or final product, while benzimidoesters apparently did not yield such ortho esters.

[1] Ber. d. chem. Ges., **31**, 1010.
[2] *Ibid.*, **40**, 3020, 3358.
[3] This Journal, **39**, 721.

I consider, however, that there is no *fundamental differ-ence* between the action of alcohols and of water in all such chemical changes. Moreover, if such an unsaturated com-pound were really intermediate in these reactions, then form-imidoester salts, $HC(=\overset{+}{N}H_2)OR$, could not be expected to yield ortho esters, because the formation of such an inter-mediate olefine derivative is here clearly impossible. But formimidoester salts are just exactly the ones found by Pin-ner to react so beautifully. Of course, we might make the assumption, using Nef's hypothesis, that a bivalent carbon derivative, $(C_2H_5O)_2C=$, is an intermediate compound in the formimidoester reactions; but I see no justification for either of these assumptions. The formation of these ortho esters, from imidoesters, is analogous to the formation of acetals from aldehydes, acids and alcohols,[1] in which reactions the formation of such an olefine derivative is impossible:

$$C_6H_5CHO + \overset{+}{H} + \overset{-}{Cl} + 2ROH \rightleftarrows$$
$$C_6H_5CHO.\overset{+}{H} + \overset{-}{Cl} + 2ROH \rightleftarrows$$
$$C_6H_5CH(OR)_2 + H_2O + HCl.$$
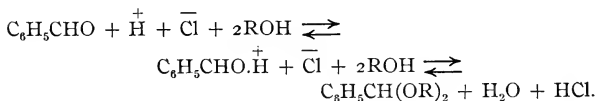
We find that benzamide, benzanilide, benzphenylhydra-zide, which cannot form any of Diel's[2] or Staudinger's[3] cor-responding intermediate ketenes, $R_2C=C=O$, discussed by Stieglitz[4] in connection with saponification, give practically quantitative yields of esters.

In view of the readiness with which such ortho esters hav-ing a group $-C(OR)_2-CH_2-$ lose a molecule of alcohol, the compound $C_2H_5OOCCH=C(OC_2H_5)_2$, obtained in the case of cyanacetic ester, most probably results, as Reiter and Hess assumed, from the loss of a molecule of alcohol from the half ortho ester of malonic acid first formed,

$$C_2H_5OCOCH_2 - C(OC_2H_5)_3 \longrightarrow C_2H_5OCOCH = C(OC_2H_5)_2.$$
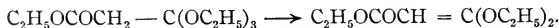
[1] Fischer and Giebe: Ber. d. chem. Ges., **30**, 3053; **31**, 545. Lapworth: Chem. News, **97**, 310.

[2] Ber. d. chem. Ges., **39**, 689; **40**, 355.

[3] *Ibid.*, **38**, 1735; **39**, 968, 3062; **40**, 1145, 1149; Ann. Chem. (Liebig), **356**, 51.

[4] THIS JOURNAL, **39**, 613.

If the olefine derivative were the intermediate product, we should expect to obtain some ortho ester, but as a matter of fact, Reiter and Weindel were never able to isolate any. This work of Pinner, then, on the reactions of imidoester salts with alcohol, gives further evidence that our point of view is worthy of further study.

Another phase of this work is of very great importance. It is clearly very desirable to determine the dissociation constants of the alcohols corresponding to those of water measured by Kohlrausch,[1] Nernst,[2] Lewis,[3] Brönsted,[4] etc.

$$H \times OH = K_w. \quad H \times O \times H = K'_w. \quad H \times OR = K_{alc.}$$
$$H \times O \times R = K'_{alc.} \quad HO \times R = K''_{alc.}$$

The facts that glass does not dissolve readily in alcohols, and that carbonic acid does not form appreciable amounts of the conducting acid esters, $HOCOOC_2H_5$, are a great help in this work,[5] while the fact that alcohol decomposes into hydrogen and aldehyde is a great disadvantage. The aldehyde is a weak acid,

$$CH_3CHO \rightleftarrows CH_2 = CHOH,$$
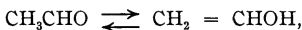
and not only would tend to act on the glass, but also tends to condense into aldol, another aldehyde which is perhaps even a stronger acid. Furthermore, both of these aldehydes may be oxidized readily into acids by the oxygen of the air. These constants for alcohol may be of very great importance, not only in a large number of oxidation and reduction reactions of the alcohols, but also in all chemical changes in alcoholic solutions in which reacting salts of weak bases or weak acids are alcoholyzed. For instance, it is obviously very important for us to know what fraction of our urazole salts is alcoholyzed when the reactions with alkyl halides are studied in alcoholic or aqueous alcoholic solutions:

[1] Z. physik. Chem., **14**, 317.
[2] *Ibid.*, **56**, 545; Z. Elek. Chem., **11**, 835.
[3] Z. physik. Chem., **55**, 449.
[4] *Ibid.*, **65**, 84.
[5] B. B. Turner: This Journal, **40**, 558.

$$\overset{+}{\text{Na}} + \overset{-}{\text{Ur}} + \text{HOC}_2\text{H}_5 \rightleftarrows \text{HUr} + \overset{+}{\text{Na}} + \overset{-}{\text{OR}}$$
$$\overset{+}{\text{Na}} + \overset{-}{\text{OR}} + \text{IC}_2\text{H}_5 \rightleftarrows \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \overset{+}{\text{Na}} + \overset{-}{\text{I}}$$
$$\overset{+}{\text{Na}} + \overset{-}{\text{Ur}} + \text{IC}_2\text{H}_5 \rightleftarrows \text{C}_2\text{H}_5\text{Ur} + \overset{+}{\text{Na}} + \overset{-}{\text{I}}.$$
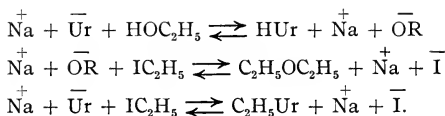
Obviously, the relationship between the alcoholysis of the sodium urazole and the velocities of the reactions of the sodium urazole and the sodium ethylate with the alkyl halide could change so much with the different urazoles and alkyl halides that greatly varying ratios of urazole ester and ether could be obtained, and this we find to be the case. In the same way an amide salt put into alcohol may be more or less alcoholyzed and hence this alcoholysis will cause a decrease in the concentration of the reacting salt:

$$\text{CH}_3\text{CO}\overset{+}{\text{NH}}_3\overset{-}{\text{Cl}} + \overset{+}{\text{H}}\overset{-}{\text{OC}}_2\text{H}_5 \longrightarrow \text{CH}_3\text{CONH}_3\text{OR} + \overset{+}{\text{H}}\overset{-}{\text{Cl}} \longrightarrow$$
$$\text{CH}_3\text{CONH}_2 + \text{ROH} + \overset{+}{\text{H}}\overset{-}{\text{Cl}}.$$
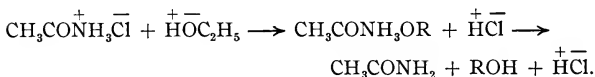
But a knowledge of the dissociation constants of the alcohols and water is of great importance in another way which I have discussed to some extent in another paper.

<div align="center">SALT CATALYSIS.</div>

When the water adds to the amide salt to form the complex cation,

$$\text{CH}_3\text{CO}\overset{+}{\text{NH}}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{C(OH)}_2\overset{+}{\text{NH}}_3 \longrightarrow$$
$$\text{CH}_3\text{COOH} + \overset{+}{\text{NH}}_4,$$
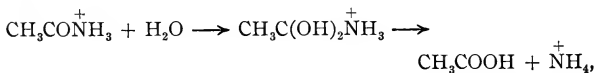
it could do so through its molecular form or the ionized portion, and the reaction velocity could be expressed approximately by the equation:

$$\frac{dx}{dt} = KC_{amide} \times C_H \times C_{H_2O} = K'C_{amide} \times C_H \times C_H \times C_{OH}.$$

Euler[1] advanced the hypothesis in 1900 that the water reacts through its ions and that salts cause the well-known salt catalysis in such reactions because they effect a corre-

[1] Z. physik. Chem., **32**, 348.

sponding change in the dissociation constant of the water. This is one of the most important questions in catalysis and work on this problem has been recorded by Arrhenius,[1] Euler,[2] Koelichen,[3] Senter,[4] Acree and his coworkers,[5] Stieglitz,[6] Reid,[7] Spohr,[8] etc. Acree and Johnson[9] considered this question and decided that the evidence was not in favor of Euler's view. Stieglitz has also taken up this question in his very important work on imidoesters and has adopted Euler's point of view, believing, with Arrhenius, that the salt cation is responsible for the salt effect. I wish to discuss this question of salt catalysis here again somewhat more fully than I did in the previous paper, especially since Lapworth,[10] one of the chief workers in catalysis, also shares in my point of view. *I believe that catalysis by salts or other neutral substances is due not so much to a change in the dissociation constant of the water as to a number of other factors of still more importance.* I consider this one of the most important phases of the mechanism of reactions, because it comes up in a large number of organic reactions, probably in most of them.

(1) I shall first discuss the evidence which leads me to believe that the views of Euler and Stieglitz are not in harmony with the facts.

(a) The physical chemical evidence obtained by Kohlrausch, Nernst, Lewis, Brönsted, and others is clearly against such a view. Stieglitz states that potassium chloride increases the velocity of hydrolysis of imidoester salts about 110 per cent per gram ion of potassium. Then the dissociation constant of water would have to increase from 1 to $\sqrt{2.10}$ or 1.45, an increase of 45 per cent in the dissociation of the water per gram ion of potassium.

Both Lewis and Brönsted have, by the use of the hydrogen-

[1] Z. physik. Chem., **1**, 110; **4**, 226; **31**, 197.
[2] *Ibid.*, **32**, 348; Ber. d. chem. Ges., **39**, 2726.
[3] Z. physik. Chem., **33**, 129.
[4] J. Chem. Soc., **91**, 460.
[5] THIS JOURNAL, **38**, 259, 489; **39**, 226; Ber. d. chem. Ges., **41**, 3208.
[6] THIS JOURNAL, **39**, 177, 467, 596, 720.
[7] *Ibid.*, **21**, 281; **24**, 397.
[8] J. prakt. Chem., **33**, 265.
[9] THIS JOURNAL, **38**, 342–4.
[10] *Loc. cit.*; Chem. News, **97**, 310.

oxygen electrode in the concentration cells $H/NaOH/Ag_2O/Ag$ and $H/NaOH/HgO/Hg$, respectively, found the values for the electromotive force to be 1.224 and 1.238 volts, which agree not only with each other, but also very closely with the value 1.232 calculated by Nernst from his direct measurements of the dissociation of water. The mean of the values of Lewis and Brönsted is 1.231, which agrees very closely with that of Nernst, the maximum error being ± 0.007 volt. Now Lewis and Brönsted calculated these values on the assumption that the dissociation constant of water,

$$H \times OH = H \times O \times H \times K,$$

does not change in the presence *of even 10/N sodium hydroxide.*

Arrhenius found that sodium chloride and potassium chloride have practically the same effect on the inversion of cane sugar. If Euler's explanation is correct, we should be able to calculate the effect of the sodium hydroxide on the dissociation of the water in Brönsted's experiment by the use of the data of Stieglitz and Arrhenius; we find that in the 4.8 N and 10.0 N solutions of sodium hydroxide *the hydrogen ion concentration should be increased nearly 300 per cent, which certainly hardly seems possible.* This would cause a change of nearly 0.02 volt in the electromotive force observed by Brönsted, whereas both his results and those of Lewis and Nernst agree to within 0.01 volt. We must remember, however, that the electromotive force varies as the logarithm of the concentration and that this method is therefore a poor one for measuring concentrations.

(*b*) If the dissociation constant of water really changes, the hydrolysis constant of the salts formed by the ester, amide, or cane sugar, and the acid, or by the ester, diacetone alcohol, etc., and alkali, would have to change correspondingly. When we consider the salt formed by the sugar and acid, we get[1]

$$C_{12}H_{22}O_{11} + \overset{+}{H} + \overset{-}{Cl} + H_2O \rightleftarrows$$
$$C_{12}H_{22}O_{11} \cdot \overset{+}{H} + H_2O + \overset{-}{Cl} \longrightarrow 2C_6H_{12}O_6 + \overset{+}{H} + \overset{-}{Cl},$$

$$\frac{dx}{dt} = K_{trans} \frac{K_b}{K_w} C_{sug} \times C_H \times C_{H_2O} = K_{trans} C_{salt\,dis.},$$
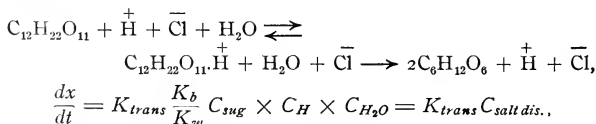
[1] Acree and Johnson: THIS JOURNAL, **38**, 306, etc.

for the velocity of transformation of the cane sugar. In this expression the factor K_w is really involved in the numerator in the C_{H_2O} and also in the denominator. These would just cancel each other and we should expect no change in the velocity constant except the *decrease* produced by the suppression of the value of C_H by the salt. But this work of Arrhenius, Spohr, Euler, Stieglitz, etc., shows that a number of salts *increase* the velocity of this hydrolysis, and others *decrease* the velocity in analogous reactions.

Koelichen found that 0.94 normal sodium thiosulphate produces a *decrease* of 4.7 per cent in the velocity of the change of the diacetone,

$$\overset{+}{K} + \overset{-}{OH} + (CH_3)_2C(OH)CH_2COCH_3 \rightleftarrows$$
$$(CH_3)_2C(\overset{-}{O})CH_2COCH_3 + \overset{+}{K} + H_2O \rightleftarrows$$
$$CH_3CO\overset{-}{CH_2} + CH_3COCH_3 + \overset{+}{K} + \overset{+}{H} + \overset{-}{OH} \rightleftarrows$$
$$CH_3COCH_3 + CH_3COCH_3 + \overset{+}{K} + \overset{-}{OH}$$
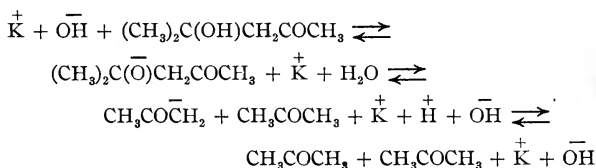
whereas Arrhenius found an *increase* of 1.8 per cent in the velocity of saponification of esters by the same concentration of this salt:

$$CH_3COOR + \overset{+}{K} + \overset{-}{OH} \rightleftarrows$$
$$CH_3C(\overset{-}{O})(OH)(OR) + \overset{+}{K} \longrightarrow CH_3C\overset{-}{OO} + \overset{+}{K} + ROH.$$
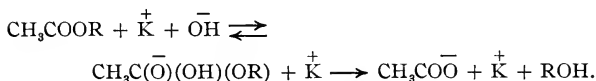
Sodium chloride, 0.94 N, *decreases* the reaction velocity of diacetone alcohol and 0.0942 N potassium hydroxide 22.4 per cent but causes only 11.8 per cent *decrease* in the velocity of saponification of ethyl acetate with 0.025 N sodium hydroxide, and an *increase* of about 65 per cent in the inversion constant for cane sugar and 0.05 N hydrochloric acid. If we assume that the catalytic influence of the salt is due to a change in the value of K_w in such equations as the above, we are led to the contradictory conclusion that the

same salt in the same concentration can both *decrease* and *increase* this value of K_w.

(*c*) If the salt effect is due to a change in the value of K_w by the cations of the salt we should expect all sodium salts in the same ionic concentration to change the velocity of a given reaction by the same amount. But Koelichen found that in 0.94 N concentrations sodium chloride, sodium nitrate, sodium thiosulphate, and sodium sulphate produce a change of —22.4, —28.5, —4.7, and +4.9 per cent. respectively, a variation that permits of no doubt as to the above conclusion.

(*d*) One of the chief reasons for doubting the validity of Euler's and Stieglitz's belief that water necessarily enters into these reactions through its ions and that salts change greatly the dissociation constants of water and alcohols was furnished by an entirely analogous reaction in which we carefully studied just this point. When alkyl halides react with urazole salts and form esters they might be considered as reacting through the dissociated portions,

$$C_2H_5I \rightleftharpoons \overset{+}{C_2H_5} + \overset{-}{I} \rightleftharpoons C_2H_4 + \overset{+}{H} + \overset{-}{I}.$$
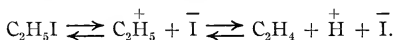
But we tested this question quantitatively,[1] experimentally and mathematically, and came to the conclusion that the alkyl halide most probably reacts as a molecule. Of course, the reactions are not identical, but they are analogous and both must be considered side by side.

2. I believe that salt catalysis is a very complex phenomenon caused by a combination of effects, a minor one of which may be the changes assumed by Euler.

(*a*) I believe that the catalyzing salts may combine with the reacting salts or substances and form still more (or less) reactive double salts or double compounds. Even if its concentration were small, this new double salt could account very readily for the *increase* in the reaction velocity if it had itself a large reaction velocity. But a *decrease* in the reaction velocity can be accounted for on this basis only by assuming a pro-

[1] Acree and Shadinger: This Journal, **39**, 244; also Acree and Johnson: *Ibid.*, **38**, 262.

portionate removal of the reacting salt or compound by the catalyzing salt in the formation of the less reactive double salts or compounds, or a change in the concentrations of the reacting substances due to a change in some equilibrium point by the added substance, or by a general change in the properties of the solutions.

An enormous amount of experimental material justifies such ideas. Jones[1] and his coworkers have shown that many double salts are present in fairly large quantities in concentrated solutions. The entire change in properties of solutions of silver nitrate, cadmium and copper salts, etc., when aqueous solutions of potassium cyanide or ammonia are added, illustrate the point beautifully; and just here it has been shown quantitatively by Noyes,[2] Whitney,[3] Goodwin,[4] Bodländer,[5] Euler,[6] Küster and Thiel,[7] etc., that these changes are brought about because of the formation of such double salts as $Ag(NH_3)_2Cl$, $K_2Cu(CN)_4$, etc.

I recall here the fact that Goldschmidt[8] has shown that hydrochloric acid, sodium chloride, barium chloride, etc., or hydrobromic acid, accelerate the reduction of nitrobenzene derivatives by stannous chloride or stannous bromide because of the formation of the more reactive double salts or complex acids, $HSnCl_3$, $NaSnCl_3$, $KSnBr_3$, $HSnBr_3$, etc. Bredig[9] has shown that in the catalysis of benzoin formation by potassium cyanide, or cyanide ions, silver cyanide, barium cyanide, etc., act as negative catalyzers because they form the double salts $KAg(CN)_2$, etc., which yield fewer cyanide ions. Slator[10] has shown that silver nitrate acts as a negative catalyzer in the reaction of thiosulphate ions with alkyl halides because it forms the less reactive or less ionized double

[1] This Journal, **19**, 83; **22**, 5, 110; **25**, 349.

[2] Z. physik. Chem., **6**, 241; **42**, 336.

[3] J. Am. Chem. Soc., **25**, 69.

[4] Z. physik. Chem., **13**, 641.

[5] *Ibid.*, **39**, 597; Z. anorg. Chem., **31**, 474; **39**, 197; **41**, 193; Ber. d. chem. Ges., **36**, 3933.

[6] Ber. d. chem. Ges., **36**, 3404.

[7] Z. anorg. chem., **24**, 57; **33**, 129.

[8] Z. physik. Chem., **48**, 435; **56**, 1.

[9] Z. Elek. Chem., **10**, 582.

[10] J. Chem. Soc., **85**, 1286; **87**, 481.

salt, $Na_2S_2O_3.Ag_2S_2O_3$. These samples serve to make clear some of the ways in which I think that positive or negative catalysis by salts or other substances may be the result, directly or indirectly, of double salt or double compound formation.

(*b*) We organic chemists have, as a rule, tried to work with dilute solutions in which *changes* in solvation, viscosity, heat of dilution, vapor tension, or osmotic pressure play a small rôle. But in a large number of the newer problems we must consider all these disturbing factors and measure their influence on the reaction velocities or reaction mechanisms. I believe that all of these factors must be considered, perhaps along with Euler's point of view, in salt catalysis.

In the last few years our physical chemists have been securing a large amount of experimental material on the influence of these various factors on the properties of solutions. Jones[1] and his coworkers have added largely to our knowledge of the relation of hydration and viscosity to conductivity. Euler[2] has shown the relation $(K—0.68)l = $ const. to hold fairly well for the relationship between the conductivity and viscosity of a solution in which K is the viscosity constant and l the equivalent conductance of the ion. Green,[3] Bingham,[4] Getman,[5] and others have recently studied the influence of fluidity on conductivity, and Washburn has brought together a very full discussion of the entire subject.[6] Now in our problems in organic chemistry we must measure both the conductivities of solutions and the reaction velocities in order to study the mechanism of the reaction and *both* of these factors are influenced by the viscosity and hydration, which are commonly ignored. Dr. Reid has found that the influence of the change in viscosity on the velocities of reactions in these aqueous alcoholic solutions is very much more marked than would ordi-

[1] For references and general literature see Carnegie Institution's Publication No. 80.

[2] Z. physik. Chem., **25**, 536.

[3] J. Chem. Soc., **93**, 2049.

[4] THIS JOURNAL, **34**, 481; **35**, 195; **40**, 277; Z. physik. Chem., **57**, 193; Carnegie Institution Publication No. 80.

[5] J. Chim. Phys., **4**, 386.

[6] Technology Quarterly, **21**, No. 4, 360.

narily be supected, and in this respect he has made a very important contribution to the theory of this reaction. This change in viscosity will probably explain to a large extent all of Goldschmidt's results. Caldwell[1] has also found that both glycerine and ethyl alcohol lower the reaction velocity of sugar inversion by nitric acid very greatly. Both of these substances decrease the fluidity of water very considerably, as Prof. Jones has found in this laboratory. Lapworth[2] has found that the addition of from 4 to 30 per cent of water to a solution of hydrochloric acid and ethyl formate or methyl acetate in acetone hardly changes the reaction velocity, the tendency to increase being nearly offset by the increased viscosity of the solution of water in acetone, as found by Jones. Kistiakowsky[3] found a similar retardent effect of alcohol in esterification.

Now the reaction velocity of the salts with other substances in solution depends upon the number of *favorable opportunities* for the union of the salt with the other substance leading to the formation of the Kekulé double salt or double molecule which yields the end products of the reaction. The velocity of the reaction will therefore vary with the number of particles and their velocity, just as does the conductivity of these salts; both the reaction velocity and the conductivity must therefore vary inversely as the viscosity. Fortunately, therefore, the relation between the reaction velocity and the concentration of the salts as determined by conductivity methods is practically independent of the viscosity in most cases studied. But each should be measured in all cases and the reaction velocity and conductivity referred to the unit of viscosity.

This salt effect will therefore be dependent on the influence of the salt on the viscosity of the solution and the change this makes in the reaction velocity. The viscosity of solutions of salts in water does not vary more than a few per cent as a rule, sometimes being positive and sometimes negative, but the salt effect is sometimes very large. Potassium chloride in gram ionic concentrations decreases the viscosity of

[1] P. Roy. Soc., **78**, A, 272.

[2] Chem. News, **97**, 248, 309.

[3] Z. physik. Chem., **27**, 250.

water only about 2 per cent[1] at 25° and yet increases the velocity of hydrolysis of cane sugar by acid over 100 per cent. It is evident then that this viscosity effect found by Dr. Reid can have only a minor influence in some cases, but should be studied in all reactions.

(c) But Armstrong[2] has in recent years put great stress on another very important phase of salt catalysis, namely, the concentrating effect of salts due to the union of the solute with the solvent. I believe that in the inversion of cane sugar in the presence of inorganic salts contact between the reacting solute, such as the cane sugar cation, $C_{12}H_{22}O_4.\overset{+}{H}$, and the large particle of hydrated salt, such as $CaCl_2.10H_2O$, cannot be to the same extent productive of favorable opportunities for inversion as a similar collision of the sugar cation with water molecules or complexes. We can readily understand that some hydrated salts might be very active in this respect and others very inactive.

The question of solvation is of very great importance in certain other phases of the work. It is becoming realized, especially from this work of Jones, Noyes and Washburn, Buchböck, Lapworth, and Goldschmidt, that the hydrogen ions are hydrated (alcoholated) to a greater or lesser extent. Now in the hydrolysis of weak bases, like amides or esters in the presence of acids, the hydrogen ions are competed for by the ester (amide), alcohol, and water. The equilibrium conditions are therefore very complex and it would be practically impossible to know the concentration of the free hydrogen ions at any moment. We have thought of using the hydrogen electrode in connection with conductivity methods, on the supposition that only the free hydrogen ions are in equilibrium with the electrode. This would enable us to get some measure of the actual amount of amide or ester salt, hydrated or alcoholated hydrogen ions, and free hydrogen ions. Denham's[3] work on aniline hydrochloride has suggested the applicability of such methods and Mr. Desha is

[1] Bousfield: Z. physik. Chem., **53**, 309.

[2] P. Roy. Soc., **78**, A, 272; **79**, 564; **81**, 80.

[3] J. Chem. Soc., **93**, 41, 424; Z. anorg. Chem., **57**, 361.

now engaged on this problem. The method, however, is complicated by many difficulties which Prof. Denham has kindly privately informed us that he, too, experienced.

(*d*) Finally, one other salt effect must be considered. The thermodynamic potential, or "activity," or driving force behind each reaction depends not only upon the substances themselves but upon the surrounding *field*. When this is changed by the addition of electrolytes or nonelectrolytes there will be a change in the corresponding thermodynamic potential and therefore in the reaction velocity, although this will in many cases be negligible. Our physical chemist colleagues must give us the aid needed here. Perhaps we shall secure aid from electromotive force measurements in reversible and irreversible reactions, such as those studied by Schoch,[1] Lewis, and many others, from heats of reaction, and other necessary data.

These and many other things influence the velocities of reactions, and much work will be necessary to clear up the many perplexing uncertainties of chemical changes.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE,
May 8, 1909.

THE ALCOHOLYSIS OR ESTERIFICATION OF ACID AMIDES.

BY E. EMMET REID.

Two of the best known reactions in organic chemistry are the esterification of acids and the hydrolysis of amides:

I. $C_6H_5CO — OH + HOC_2H_5 = C_6H_5COOC_2H_5 + H_2O$,

and

II. $C_6H_5CO — NH_2 + HOH = C_6H_5COOH + NH_3$.
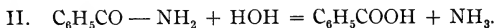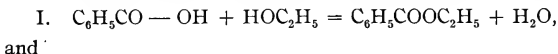
If, now, as appears from the formulae above, benzoic acid and benzamide are analogously constituted derivatives of

[1] THIS JOURNAL, **41**, 208, 232.   J. Chem. Soc., **29**, 314.   Trans. Am. Elec. Chem. Soc., **11**, 135.

water and ammonia, H—OH and H—NH$_2$, which are un-doubtedly analogous in many of their reactions, and if water and alcohol are analogous, then alcohol should act on benz-amide to give the ester:

III. $C_6H_5CO — NH_2 + HOC_2H_5 = C_6H_5COOC_2H_5 + NH_3$.

When I mentioned to Professor Acree my intention of try-ing this reaction, he at once said that he had predicted it from his point of view of catalysis, particularly with reference to amide salts, and that it would be found to go in a manner similar to the reactions of hydroxylamines, hydrazines, and amines on amides and analogous substances, and to Pinner's formation of ortho esters from imidoester salts.   My experi-ments have shown results in harmony with his views.

Reaction (1) is commonly accelerated by a catalytic agent such as hydrochloric acid.   Accordingly some *p*-nitrobenz-amide was dissolved in absolute alcohol and dry hydrochloric acid passed in.   After a few minutes' warming, on pouring the mixture into water, a precipitate was obtained which, on being freed from unchanged amide by washing with hot water, showed the melting point, 57°, and other properties of ethyl *p*-nitrobenzoate.   Hence the above reaction does take place and an amide may be esterified under the same conditions, and with the same facility, as the corresponding acid.   This appears as the reversal of the well-known reaction by which an amide is made from the ester and ammonia.

Quantitative experiments showed that at 50° the reaction proceeded at a rate convenient for measurement.   Accord-ingly measurements of the reaction velocity were undertaken, using benzamide and the three nitrobenzamides in absolute alcohol, with hydrochloric acid as a catalytic agent.   Some little work has been done also in alkaline solution, but so far without definite results.   Since beginning this work I have come across that of Guareschi,[1] who heated benzamide and phenol to the boiling point of the mixture and got phenyl benzoate among other things.   His point of view and method of work were entirely different from mine.

[1] Ann. Chem. (Liebig), **171**, 141.

A considerable amount of work has been done, but before the subject can be cleared up it must be taken up in a more comprehensive way and the work extended in a number of directions. In order to reserve the field for myself until some, at least, of this work can be done, I have thought best to publish some of the results so far obtained.

Method of Work.

The required amount of the amide was weighed into a flask holding about 12 cc. These flasks were specially blown with long narrow necks. Beginning with Series VI., test tubes were used. These test tubes were heated with dilute hydrochloric acid for two days before use. They serve well for this purpose for, on account of the thinness of the glass, they may be put into the flame directly and can then be cooled quickly. After the solid was weighed in, the test tube was drawn down to a narrow neck through which the pipette passed. The alcoholic hydrochloric acid was kept for at least three minutes in a pipette jacketed with water at 50° C. After running in this solution the flask was corked up, or the test tube sealed off, and plunged, with vigorous shaking, into the water bath at 50°. These operations, altogether, usually required less than one minute. The amide dissolved quickly. The tube was drawn off at such a point as to leave little air space over the solution. To stop the reaction the contents of the flask, or test tube, were poured into cold water containing nearly enough caustic soda to neutralize the acid present.

The ammonia from each sample was distilled with magnesium hydroxide into N/10 hydrochloric acid. The excess of acid was titrated back with N/10 alkali, with cochineal as indicator. When the neutral point was reached the burette containing the acid was also read and an unknown amount of the acid run into the flask containing the distillate. This was again neutralized with the alkali and both burettes again read. This process was repeated. Thus the estimation of the ammonia in the distillate was made to depend on three

independent titrations. These usually agreed quite closely. The mean of the three was always taken.

The magnesium hydroxide was made each time by adding 5 cc. of 5 N magnesium chloride and 5 cc. 2.5 N caustic soda to the nearly neutralized sample in the distillation flask. Experiment showed that when weighed samples were distilled the usual time, 70 minutes, under the usual conditions, with magnesium hydroxide, 0.25, 0.5, and 0.6 per cent of benzamide, meta-, and paranitrobenzamides, respectively, were decomposed. Accordingly, x, the percentage of decomposition found, was diminished by 0.25, 0.5, or 0.6 per cent of 100—x, according to the amide used.

The amides used were carefully purified by repeated crystallization, the last time from conductivity water. The alcohol used in Series I. to III. was commercial absolute alcohol of about 99.5 per cent. The other series were made with 99.78 per cent alcohol, prepared by double distillation from lime. The strength of the alcohol was determined by the kerosene test.[1] The dilute alcohols were made by adding weighed amounts of water to weighed amounts of the 99.78 per cent alcohol into which dry hydrochloric acid had been passed. A common stock solution was made up for each series. A portion of this was measured at 50° from the pipette in the usual way, weighed, and titrated to obtain the value of A for that series.

The great influence of water on the speed of the reactions was not considered in the earlier work, and sufficient care was not taken to prevent its absorption. This may account for some of the erratic results. The temperature was 50°.05 C. with a variation of one or two hundredths either way, except in Series XII. and XIII., in which it was 50°.19 C. The volume of the sample was 10.34 cc. except in Series XII. and XIII., in which it was increased to 20.67 cc. on account of the smaller solubility of the benzamide in water.

The analytical data have been substituted in the usual formula for a bimolecular reaction,

$$K = \frac{2.3025}{(A-B)t} \log. \frac{(A-x)B}{(B-x)A}.$$

[1] Andrews: J. Am. Chem. Soc., **30**, 353.

A is the concentration of the hydrochloric acid, B that of the amide used, both in terms of volume molecular normal, while t is the time in minutes, and x the corrected percentage of the amide decomposed. Since A and B appear in like powers in both the numerator and denominator of the fraction in the last portion of this expression, for convenience of calculation B was taken as 100 per cent and A as the proper multiple of this.

The closeness with which the reaction obeys the bimolecular formula may be seen from the values of K taken from Series VI. and VII.:

Series VI.	1084	1079	1084	1074
Series VII.	1046	1043	1044	1036

The agreement in Series XI. and XII. for benzamide is equally good. These are the only series made under the best conditions. The amounts of ammonia found in some of the shorter period samples, particularly for benzamide, are too small for good analytical work. One per cent decomposition gives only 0.5 mg. ammonia or 0.3 cc. N/10 acid. In some of the analyses given the amount of N/10 acid neutralized was only about 0.60 cc. The errors of titration, etc., may be a considerable per cent of this small amount. In all of the tables the real value of K is multiplied by 1,000,000 to avoid decimals.

The formation of ethyl chloride diminishes the strength of the acid somewhat, but this effect is considerable only in long time periods, and even in these periods, with amides which decompose rapidly, the most of the amide has already reacted before the acid loses much of its strength. Samples of the acid used in Series VI. and VII. were heated for 12 and 36 hours in sealed tubes at 50° and were found to lose strength at the rates of 0.27 and 0.26 per cent, respectively, per hour. In the present work it has not been thought worth while to introduce corrections for this into the calculations, though nearly all the values of K for long time periods show a falling off which may be accounted for in this way. Cain's[1]

[1] Z. physik. Chem., **12**, 751.

work indicates a more rapid formation of ethyl chloride at 50° though none of his work was done at this temperature. The conditions of his experiments were, however, quite different.

The first thing to be found out in the experiments was whether the reaction was really of the second order. Determinations running all the way from 2 to 75 per cent decomposition show that the equation holds over at least this range. The next matter was to contrast the different amides with each other with the same and with different concentrations of acid. Series were run with concentrations of acid from 0.4 to 3.7 N, in order to determine the influence of this factor on the velocity.

Series I.—A 3.640 N, B 0.1934 N, Alcohol 99.5 per cent.
   m-Nitrobenzamide.

t	30	60	90	120	240	480	Average.
x	7.32	13.07	19.50	26.04	44.72	68.77	
K	697	643	665	699	686	702	682

   p-Nitrobenzamide.

x	8.58	15.79	23.06	29.14	48.26	73.54	...
K	832	790	805	792	774	787	797

Series II.—A 2.870, B 0.1934, Alcohol 99.5.
   m-Nitrobenzamide.

t	90	120	150	240	420	450	480	510	Av.
x	...	...	...	43.76	60.51	64.66	...	...	
K	...	...	...	849	800	827	...	...	824

   p-Nitrobenzamide.

x	21.76	27.76	33.39	45.07	...	69.82	71.28	73.83	
K	958	950	956	942	...	955	932	944	950

Series III.—A 0.3967, B 0.2903, Alcohol 99.5.
   Benzamide.

t	90	120	240	480	16h	24h	48h	Average.
x	1.42	2.12	3.61	6.41	10.04	10.55	36.16	
K	404	(454)	391	(356)	407	398	404	400

For brevity we will designate the constants (K) for meta- and paranitrobenzamides as K_m and K_p, and that for benzamide as K_b. From Series I., $K_p/K_m = 1.17$ and from Series II., 1.15. These values are very near to the ratio

of the hydrolysis constants for the same amides, namely,
1.20.[1] Goldschmidt[2] finds for the esterification of meta-
and paranitrobenzoic acids the ratio $K_p/K_m = 1.20$.

For further discussion the average values of the various
constants are brought together in the following table, several
being taken from the series given below. The first column
gives the number of the series from which the results are taken.
Under N is the strength of the acid in such series and under
V the reciprocal of N. The series are so arranged that V,
the volume of solution containing a gram molecule of hydro-
chloric acid, increases from top to bottom. In the next col-
umn is found the molecular conductivity, and in the last three
columns are given the quotients obtained by dividing the
several values of K by the molecular conductivity.

It appears that K_m/K_b is 4.5 with 1.5 N acid, but only
3.7 with 1 N acid and even lower with weaker acid. One
determination, not included in the series given, indicates
that this ratio is much higher with the 3.6 N acid. K_m/K_b
for the hydrolysis of these two amides in water solution is
0.94, the benzamide being hydrolyzed even faster than the
m-nitrobenzamide.

Table I.

Series.	K_m.	K_p.	K_b.	N.	V.	$m.c.K$	$m/m.c.$	$K_p/m.c.$	$K_b/m.c.$
I.	682	797	...	3.64	0.275	6.2	110	129	..
II.	825	950	...	2.87	0.348	7.0	118	136	..
IV.	987	...	220	1.52	0.658	8.6	115	...	25
VI.	1080	...	288	1.09	0.911	9.5	114	...	30
III.	....	...	400	0.397	2.52	12.3	...	...	33

That benzamide, a derivative of ammonia, is a real base
is shown by the existence of many of its salts. It forms
well-defined salts even with weak acids. Its oxalate, tar-
trate, and succinate have recently been prepared by Henle.[3]
It will exist then in hydrochloric acid solution in four forms,
the amide, its hydroxide, its hydrochloride, and the cation,
$C_6H_5CON\overset{+}{H_3}$, derived either by the dissociation of the salt

[1] Remsen and Reid: THIS JOURNAL, **21**, 281.
[2] Z. Elek. Chem., **15**, 9.
[3] Ber. d. chem. Ges., **38**, 1373.

or by the direct combination of the hydrogen ions with the free base. The case of acetamide has been thoroughly worked out mathematically and the conclusions verified experimentally by Acree and Nirdlinger.[1] They conclude that the rate of decomposition would be infinitesimal if the amide itself were the reacting substance. The same reasoning applies to the hydroxide of the amide as it is also present in pure water solution in somewhat the same proportion to the amide as it is in acid solution. They show that if the undissociated salt were the reacting substance the reaction velocity, K, should be inversely proportional to the concentration of the acid, while if the complex cation is the chief, or sole, reacting substance the velocity of the reaction must conform to the well known bimolecular reaction formula.

That the bimolecular formula is applicable may be shown in the following somewhat different manner. Assume that the complex cation is the reactive substance. Then the re-action will be a monomolecular one with regard to this cation and hence will obey the monomolecular law, $\frac{dx}{dt} = yk$, in which y is the amount of this ion at the time, t. We do not know anything about the magnitude of y, but we do know that it is a certain fraction of the amount of amide present at that time. If B is the original concentration of the amide, the amount of it present at the time, t, will be $B - x$, so we may put $y = (B - x)s$ in which s is this fraction. Now s in this expression involves two things, namely, the affinity constant, or salt-forming power, of the amide and the con-centration of the hydrogen ions at that time. The affinity constant being constant for a given amide, we may replace s by $[\overset{+}{H}]b$, in which b is a constant for the amide. This as-sumes that the equilibria between the amide, its salt, and the ions of the salt are instantly adjusted, as is usually the case with that class of equilibria. But $[\overset{+}{H}]$, the concentra-tion of the hydrogen ions, equals $a(A - x)$ in which $(A - x)$ is the concentration of acid and a is the fraction of the acid

[1] This Journal, **38**, 489.

which is dissociated at that time. If the conditions are such that the percentage of ionization of the acid does not change much during the reaction, a is sensibly constant. Then we may put $\frac{dx}{dt} = ab(A - x)(B - x)k = (A - x)(B - x)K$, as the product of three constants is a constant. Reactions of alkyl halides, acylhalogenaminobenzene derivatives, and oximes have been treated by Acree and his coworkers[1] in a precisely analogous manner.

In the above we may use the value of a as determined in pure water solutions of hydrochloric acid, provided the amide present is an extremely weak base or is present in very small quantities relative to the acid. Acree and Nirdlinger saw clearly the importance of a knowledge of the strength of the amide base so as to be able to calculate the amount of salt formed and the change in dissociation of the acid. They proposed to measure this strength so as to be able to make these calculations. They did make a few measurements as to the amount of salt formed and found it to be only a few per cent of the amount of amide present.

That the hydrolysis of amides conforms to the bimolecular reaction formula was first shown by Ostwald[2] for acetamide and ten years ago by Remsen and Reid[3] for benzamide and twenty-four substituted benzamides, and recently by Crocker[4] for seven fatty amides. None of these authors were particularly concerned with the mechanism of the reaction. Acree and Nirdlinger were the first to study it with particular reference to intermediate compounds, such as salts and their ions. By varying the concentrations of the amide and the acid they obtained considerable evidence that the complex cations are chiefly, if not solely, concerned in the reaction.

This is here accepted as the mechanism of hydrolysis. For the history and development of this theory as applied to catalysis in general, and for full references to the articles of all who have worked upon it the many papers on catalysis

[1] This Journal, **38**, 258 and 489; **37**, 410; and **39**, 228, 237–47.
[2] J. prakt. Chem., **135**, 1.
[3] This Journal, **21**, 281; **24**, 397.
[4] J. Chem. Soc., **91**, 952.

by Professor Acree and his students[1] must be consulted. It remains here to adapt this theory to the facts brought out in Table I., particularly as relates to the different behavior of benzamide and the nitrobenzamides.

Benzamide, being decidedly basic, will combine quite largely, relatively to the nitrobenzamides, with the hydrogen ions, even with a moderate excess of acid and a moderate concentration of hydrogen ions, and hence an increase in the concentration of the acid will not produce a proportionate increase in the concentration of the complex ion. Hence its reaction rate, which depends on the amount of the complex ion, will not increase proportionately with increased acid concentration. That it does not appears from the last column of the table. The nitrobenzamides, being far weaker bases, will, in a given concentration of acid, form far less of these complex ions, but, the amide concentration remaining the same, the amounts of these complex ions in various concentrations of acid will be closely proportional to the concentration of the hydrogen ions, even over a wide range of dilution. The ionization of the acid as found in the pure solvent may be used with little error. Thus the conductivity of hydrochloric acid in water increases only slightly when it is diluted from one volume to two but the conductivity of acetic acid nearly doubles for the same dilution. This all follows from the application of the mass law to these equilibria, as has been discussed by Acree, Bredig, Stieglitz, Lapworth, Goldschmidt, and others.

That a considerable combination of *p*-nitrobenzamide with something in the solution does take place with high concentrations of acid, and only with high concentrations, is shown by the fact that the desired amount of this amide dissolved quickly in the concentrated acid of Series I. and II., but with the same volume of the 0.4 N acid of Series III., long shaking effected solution of only a fraction of this amount. The use of this amide had to be discontinued on this account.

Data as to the ionization of hydrochloric acid in alcohol

[1] This Journal, **28**, 370; **37**, 71, 410; **38**, 258, 489, 746; **39**, 145, 226, 300; J. Am. Chem. Soc. **30**, 1755; Ber. d. chem. Ges., **41**, 3199.

are scarce, and the value of the older work has been made doubtful by the recent work of Goldschmidt[1] showing the great influence of even small amounts of water on the conductivity of such solutions. The following data as to the conductivity of hydrochloric acid in alcohol have been taken from the work of Kablukoff,[2] (1) $v = 0.55$, $\mu = 8.11$; (2) $v = 0.98$, $\mu = 9.40$; (3) $v = 1.17$; $\mu = 10.59$; (4) $v = 2.37$, $\mu = 13.24$. These are plotted on the accompanying diagram and a smooth curve drawn, extending to the origin, compromising the several determinations. From this curve the values
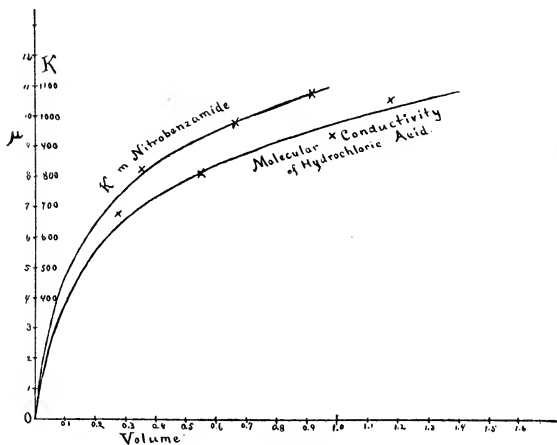
Fig. I.

for molecular conductivity for the required volumes have been taken off and inserted in the above table. The quotients in the following columns show that the rates of alcoholysis for meta- and paranitrobenzamides are very nearly proportional to the hydrogen ion concentration in the various solutions. The low values for the constants (K) of the first series may be, at least partly, explained by the fact that this

[1] Z. Elek. Chem., **15**, 6.
[2] Z. physik. Chem., **4**, 429.

solution of hydrochloric acid in alcohol was made several weeks before it was used and was not guarded from the moisture of the air. All others were used as soon as possible after making. The values of the several constants are plotted and a curve drawn for comparison. If the constants for the nitro-amides follow the curve, those for benzamide can not.

From Series IV. below it appears that the nitro group in the ortho position exercises the same remarkable retarding influence as it does in hydrolysis of amides and in esterification of acids.

After these first three series had been made the work of Goldschmidt[1] and Lapworth[2] on the influence of small quantities of water on esterification velocities of acids raised the question as to what that influence might be on the esterification velocities of amides. Series IV. and V. were run to decide this question. The group of five series following was made to carry this over a greater range.

Series IV.—A 1.520, B 0.2903, Alcohol 99.78.
  Benzamide.

t	60	120	240	480	Average.
x	2.19	3.90	7.61	14.76	
K	(245)	219	219	221	220

  m-Nitrobenzamide.

x	8.74	16.53	29.11	48.35	
K	1013	1008	972	955	987

  o-Nitrobenzamide.

x	...	...	1.29	3.03	
K	...	...	36	42	39

Series V.—A 1.502, B 0.2903, Alcohol 97.67.
  m-Nitrobenzamide.

t	60	120	240	480	Average.
x	6.67	12.81	23.33	40.87	
K	770	770	753	762	764

[1] Z. Elek. Chem., **15**, 4, and Z. physik. Chem., **60**, 749.
[2] J. Chem. Soc., **93**, 2187.

Series VI.—A 1.094, *B* 0.2903, Alcohol 99.78.
   Benzamide.

t	60	120	240	480	Average.
x	2.13	3.58	7.17	14.07	
K	(331)	282	288	295	288

   m-Nitrobenzamide.

x	6.56	12.96	24.02	41.12	
K	1084	1079	1084	1074	1080

Series VII.—A 1.0909, *B* 0.2903, Alcohol 99.48
   Benzamide

t	60	120	240	480
x	2.09	3.61	7.06	13.85
K	324	280	282	290

   m-Nitrobenzamide.

x	6.77	12.56	2 3.23	40.00
K	1046	1043	1044	1036

Series VIII.—A 1.085, *B* 0.2903, Alcohol 98.77
   Benzamide.

t	240	480	960	1920
x	6.27	13.17	24.20	48.28
K	251	276	275	282

   m-Nitrobenzamide.

x	20.81	35.43	57.25	. . .
K	923	946	896	. . .

Series IX.—A 1.070, *B* 0.2903, Alcohol 97.57
   Benzamide.

t	120	240	480	960	1920
x	. . .	5.83	12.21	22.55	40.54
K	. . .	236	258	257	269

   m-Nitrobenzamide.

x	9.28	17.79	30.81	48.50
K	768	782	756	698

Series X.—A 1.047, *B* 0.2903, Alcohol 93.93.
   Benzamide.

t	240	480	960	1920
x	4.81	9.64	18.64	33.99
K	198	204	211	218

   m-Nitrobenzamide.

x	11.46	21.18	37.02
K	492	489	456

Series XI.—A 1.0068, *B* 0.2903, Alcohol 88.59.

	Benzamide.		*m-Nitrobenzamide.*	
t	480		480	960
x	7.82		14.99	7.05
K	170		344	340

The values of the constants for benzamide, K_b, as found for the 8- and 16-hour periods, and those for *m*-nitrobenzamide, K_m, for the 4- and 8-hour periods, have been considered in making out the following table. From the trend of these, when plotted against the percentage of water present in the various series, 296 has been assumed as the value of K_b in perfectly anhydrous alcohol and 1120 as the value of K_m in the same. It is intended to verify these by actual experiment with perfectly anhydrous alcohol. In the first column is given the percentage of water calculated from the weights of water and alcohol present, in the next the molecular percentage of water, then the value of the constant for benzamide and the percentage of retardation, then the same for *m*-nitrobenzamide.

Table II.

Per cent water.	Mol. per cent.	K_b.	Per cent ret.	K_m.	Per cent ret.
0.00	0.00	296	0.0	1120	0.0
0.22	0.59	291	1.7	1080	3.7
0.52	1.32	286	3.4	1042	7.0
1.23	3.05	276	6.7	934	16.6
2.43	5.94	258	12.8	769	31.4
6.07	13.92	207	30.1	491	56.1
11.41	24.55	170	42.5	342	69.5

These results show the enormous influence of water on the velocity of the decomposition of the amides. They are based on the amount of ammonia found, and hence of amide decomposed, regardless of whether it went into the ester or into the acid. The effect of the water is quite different in amount for the two amides. The effect of water on the esterification of amides is quite like its effect on the esterification of acids.

In order to compare these results with the effect of water on the esterification of acids, the values of "K'''" given below

have been taken from Goldschmidt's work.[1] The units are different but they are comparable among themselves. They were obtained with very much weaker acid than was used with the amides, hence are comparable only in a general way. The amounts of water are those used by Goldschmidt, calculated in percentages by weight. The data for the amides are taken directly or by interpolation from Table II., above. Goldschmidt's values of K' are taken for the shortest time periods, the ones that suffer least from the accumulation of water during the reaction. R_b, R_m, and R_a are the retardations of the esterification of benzamide, *m*-nitrobenzamide, and benzoic acid, respectively, produced by the stated amounts of water. These are calculated as percentages of the maximum rates.

Table III.

Water	0.00	0.22	0.45	0.90
K_b	296	291	287	281
R_b	. .	1.7	3.0	5.0
K_m	1120	1080	1051	989
R_m	. .	3.7	6.2	12.1
K'	220	188	148	104
R_a	. .	14.5	32.7	52.7
R_m/R_b	. .	2.2	2.1	2.4
R_a/R_m	. .	4.0	5.3	4.3

It appears from this comparison that the effects of like amounts of water on the rates of esterification of these three compounds are strictly comparable. It is several times greater with one than with another but the effect seems to be of the same order in all three cases and the proportionality is maintained as the amount of water increases. This accords perfectly with the theory if we assume, with Kastle, Bredig, Lapworth, Stieglitz, and Acree, that the hydrogen ion unites with the benzoic acid to form a complex cation, as it does in the case of the amides. For much evidence on this view see the article of Acree and Johnson.[2] The weaker the base of a salt, the greater the amount of its hydrolysis, or decomposition, by a given amount of water. This is well

[1] *Z. physik. Chem.*, **60**, 749.

[2] This Journal, **38**, 258.

understood in the case of such salts as aluminum and antimony chlorides. If benzamide, *m*-nitrobenzamide, and benzoic acid all form hydrochlorides, these salts will all be more or less unstable and will be decomposed by water, the amount of the decomposition decreasing in the order given, since *m*-nitrobenzamide is a weaker base than benzamide, and benzoic acid, as a base, is far weaker still. The ions of a salt are always in equilibrium with the undissociated salt. As the velocity of the reaction depends on the concentration of the cation of this salt, it will ultimately, though not directly, depend on the amount of the salt present in the solution, undissociated as well as dissociated. That alcohol may decompose salts in an analogous way is generally assumed. From recent work of Lapworth,[1] it would appear that alcohol is far less efficient than water in this reaction.

After making these experiments, it appeared interesting to compare the effect of alcohol on the rate of hydrolysis with the influence of water on the rate of alcoholysis. Accordingly the following determinations were made with benzamide. Only half the usual concentration of the amide could be used on account of its smaller solubility in water.

Series XII.—*A* 0.9600, *B* 0.145, Water 100 per cent.

t	20 h.	36 h.	38 h.	60 h.	Average.
x	22.16	37.24	38.96	53.84	
K	(225)	232.5	233.8	235.3	234.5

Series XIII.—*A* 0.9665, *B* 0.1451, Alcohol 8.05, mol. per cent 5.67.

x	19.29		34.25	47.85	. . .
K	(188)		196.4	195.6	196.0

From the average of the 38- and 60-hour experiments the retardation produced by the alcohol is 16.4 per cent. The two 20-hour samples were heated at a different time and, by an accident, the temperature went too low for a part of the period. Hence they are not to be compared with the others as to the value of K, but when compared with each

[1] J. Chem. Soc., **93**, 2187.

other, they show a retardation of 16.2 per cent. I have since found that a like amount of alcohol retards the hydrolysis of benzamide by barium hydroxide to about the same extent. In the reaction mixture of every sample of Series XIII. ethyl benzoate was easily detected. Hence esterification, or alcoholysis, of the amide goes on in presence of a very large excess of water.

If on a diagram we plot the rate of decomposition of benzamide, whether alcoholysis or hydrolysis, with regard to the amounts of water and alcohol present, the curve is seen to sag rapidly at each end (Fig. II.) If molecular percentages
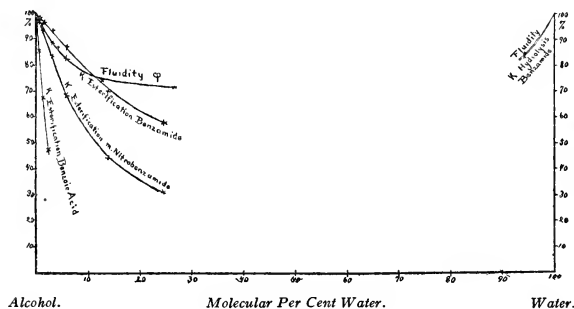
Alcohol.   *Molecular Per Cent Water.*   *Water.*
Fig. II.—Influence of water on rates of reactions.

are considered, the two ends of the curve show a marked resemblance to each other. In a conversation with Professor Jones, there was brought out the resemblance of this curve to the fluidity curve of mixtures of alcohol and water as drawn by Jones and Carroll.[1] Accordingly viscosity measurements were made on the acid solutions used in Series XII. and XIII. These did not contain the amide. Measurements were made with an Ostwald viscometer.[2] The viscosities at 50° for the two solutions were found to be 0.00590 and 0.00699. Taking the reciprocals of these as fluidities, we find that the fluidity of the water-alcohol solution is 84.4 per cent of the fluidity

of the pure water solution. Thus the presence of this quantity of alcohol reduces the fluidity 15.6 per cent and retards the reaction 16.3 per cent. The increase in viscosity apparently accounts for much of the decrease in the speed of the reaction. The close numerical agreement in this case is regarded as accidental. That there are other important factors is certain. This will be considered more fully further on.

The solutions with which Series VI. to XI. were made had been used up, but a series of others were prepared of nearly the same proportions, strength of acid, etc. A 10 cc. sample of each was taken and 363.3 mg. of benzamide, the amount used in the regular determinations, dissolved in it. The viscosities of these mixtures were measured at 50°. From these measurements the viscosity for no water was found by extrapolation. The amounts of retardation are taken from Table II. above, either directly or by interpolation. The concentration of the amide was in each case 0.295. The results are tabulated in Table IV.

Table IV.

Per cent water.	Mol. per cent.	Conc. HCl.	Viscosity.	Fluidity.	Per cent dec. of φ.	Per cent retard.
0.00	0.00	1.070	0.00957	104.5	0.0	0.0
0.22	0.59	1.072	0.00975	102.6	1.8	1.7
0.44	1.09	1.068	0.00993	100.7	3.6	3.1
1.29	3.20	1.048	0.01082	92.4	11.6	7.0
1.71	4.26	1.065	0.01100	90.0	13.0	9.9
2.42	5.94	1.028	0.01152	86.0	17.7	12.8
6.00	12.75	1.075	0.01292	77.6	26.0	29.8
12.50	27.00	1.129	0.01341	74.6	28.6	45.0

As we pass from alcoholic to water solutions, hydrolysis gradually replaces alcoholysis. When the water molecules begin to be a considerable proportion of the whole number, this partial substitution of K_h, the hydrolysis velocity, for K_a, the alcoholysis velocity, will produce a sensible lowering in the average velocity. As we pass from the one medium to the other there is a change in the degree of dissociation of the hydrochloric acid, and a general shifting of all equilibria. The concentration of the amide salt and its degree of dissocia-

tion must change. All of these changes are, doubtless, more or less gradual, depending on the gradual increase in the proportion of water molecules. In the case of the amides here worked with, for small additions of water to alcohol, or *vice versa*, the changes in viscosity seem able to account very largely for the observed changes in reaction velocities. With much larger additions, changes in viscosity continue to account for an important proportion of the observed retardations.

The extensive and important work of H. C. Jones and his coworkers[1] on viscosity in relation to conductivity of electrolytes in mixtures of solvents has shown the great influence of viscosity on conductivity. The recent work of Green,[2] in which the viscosity of conducting solutions was intentionally increased, shows the same. The above results suggest that a knowledge of the viscosity of the media in which reactions take place is fundamental to an estimate of the real value of the velocity constants. Thus at 50°, with hydrochloric acid, for benzamide, K_h for pure water is 234, while for alcoholysis in pure alcohol, K_a is 296. Plainly these constants are not directly comparable since the hydrolysis was measured in a solution whose viscosity was 0.00590, while the viscosity with which the molecules had to contend in the alcoholysis was 0.00957. From now on I intend measuring the viscosity of every solution in which I measure a reaction velocity. I hope to study the influence of viscosity on these and other reactions.

In the case of an amide in the presence of both alcohol and water, alcoholysis and hydrolysis go on parallel. Thus we have the two reactions:

$$C_6H_5CONH_2 + H_2O = C_6H_5COOH + NH_3,$$

and

$$C_6H_5CONH_2 + HOC_2H_5 = C_6H_5COOC_2H_5 + NH_3.$$
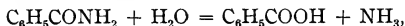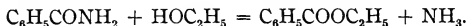
So far only a little work has been done on the comparative rates of the two reactions in mixtures of alcohol and water. With a sample of 498.4 mg. of *m*-nitrobenzamide which

[1] "Viscosity and Conductivity," H. C. Jones and others: Carnegie Institution Publication No. 80. Also numerous journal articles.

[2] J. Chem. Soc., **93**, 2049.

was heated seven days with the 93.93 per cent alcohol of Series X., the ammonia found showed 86.97 per cent decomposition of the amide. The ester and acid were extracted with ether and the acid titrated. This accounted for 4.58 per cent. The ester was heated with water and allowed to solidify in a lump. This, after drying, weighed 489 mg. Its melting point was low, and it was again heated with water. This brought its melting point up to 42°, the correct value. The water extract was distilled with strong caustic soda, and ammonia corresponding to 10 mg. of the amide was found. Subtracting 10 from 489 gave 479 as the correct weight of the ester. This corresponds to 82.97 per cent of the amide, making 86.89 per cent of the 86.97 per cent of the amide decomposed. This is of interest as showing that alcoholysis is a clean reaction and that alcoholysis and hydrolysis may be studied in the same solution and their rates compared. The ratio of ester and acid found in this experiment is not to be taken as representing the true ratio of the rates of their formation, as in the long time which this sample was heated some of the ester may have been saponified, or the reverse.

By extracting the acidified distillation residues and titrating the extracted benzoic acid, the amounts of hydrolysis in some of the samples of Series X. and XI. were determined. Allowance had to be made for the ethyl benzoate saponified during the distillation with the magnesium hydroxide. As this allowance was considerable and somewhat uncertain, the results are only approximate. The results give the hydrolysis in percentages of the total amide decomposed. For the four benzamide samples of Series X. with 13.92 molecular per cent of water, these values are 11.6, 11.5, 14.2, and 13.0, average 12.6 per cent; and for one sample of Series XI. with 24.55 molecular per cent of water present, 17.5 per cent; that is, the alcoholysis went on 7.9 times as fast as the hydrolysis in the first case, and 4.6 times as rapidly in the other.

In order to explain the enormous influence of small amounts of water on the velocity of esterification Goldschmidt[1] and Lapworth[2] have recently put forward theories which they

[1] Z. Elek. Chem., **15**, 4.
[2] J. Chem. Soc., **93**, 2187.

support with mathematics and a mass of experimental data. Goldschmidt assumes that the reactive substance in catalysis of this sort is the ion $C_2H_6O\overset{+}{H}$, formed by union of the hydrogen ion with a molecule of alcohol. According to his theory, when water is introduced, the $\overset{+}{H}$ hydrogen ion leaves the alcohol and goes to the water to form $H_2O\overset{+}{H}$ ions. Thus the amount of this change depends on the amount of water added.

Lapworth assumes that the $\overset{+}{H}$ ions are the active agents in such reactions and that as water is added these combine with water molecules to form $H_2O\overset{+}{H}$ ions which are inactive so far as esterification, etc., are concerned. He concludes that real $\overset{+}{H}$ ions are extremely scarce in water solution.

The extensive work of Jones[1] and his students on hydrates in solution all goes to show that salts are commonly hydrated in solution and that ions are probably still more hydrated. The work of Washburn[2] serves to emphasize the hydration of ions. Carrara[3] recognizes the possibility of alcoholation as well as hydration of ions. The work of Jones further shows that in alcohol the salts are *solvated* as they are in water. The reciprocal relations of water and alcohol are beautifully shown in Plate XVI. of the work of Jones and Anderson[4] on neodymium chloride in mixtures of methyl alcohol and water. In water solution certain bands exist, in alcoholic solution, certain others, distinct in character and location. They say: "In every case where the alcoholic solution has a strong band . . . we begin to see traces of this band when the proportion of alcohol in the mixture reaches 50 per cent." "The band belonging to the aqueous solution may be seen very clearly even in the strip corresponding to the 2.6 water solution. . . . " "On Plate XVI. the two sets of bands coexist, the bands due to the aqueous solution decreasing, while those belonging to the alcoholic solu-

[1] Carnegie Institution Publication, 60, also numerous journal articles.
[2] J. Am. Chem. Soc., **31**, 322.
[3] Ahrens' Sammlung, **12**, 413 (1908).
[4] THIS JOURNAL, **41**, 185, 276.

tion increase in intensity with decrease in the percentage of water; . . . the two sets of bands have about half their full intensity in a solution containing about 8 per cent. of water." Plate III. for cobalt chloride in mixtures of ethyl alcohol and water shows the rapid disappearance of the distinctive alcohol bands with increasing additions of water. Kohlrausch, Werner, and others have regarded hydration, or something of the sort, as a necessary part of the mechanism of dissociation in solution. A. A. Noyes has held somewhat analogous views.

Considering the work and ideas of all these investigators, together with the cation theory of catalysis, I am inclined, as a working basis, to combine these ideas in the following manner. From what has been said above it will be seen that all of the ideas are borrowed, but the combination may be suggestive. We will consider all, or practically all, hydrogen ions in water solution to be hydrated. From the great mobility of the hydrogen ion and from the work of Jones and Getman[1] on organic acids, the amount of water combined with this ion must be small, say, $1 H_2O$, making $H_2\overset{+}{O}H$. In alcohol the hydrogen ion would be alcoholated forming, say, $C_2H_6\overset{+}{O}H$. In mixtures of water and alcohol some of the hydrogen ions would be hydrated and the others alcoholated. Since, as is shown by the work of Jones and Anderson, the tendency to hydration is much greater than the tendency to alcoholation, with equal numbers of water and alcohol molecules there would be more of the hydrated than of the alcoholated hydrogen ions. In the case of neodymium chloride in methyl alcohol and water, the tendency towards hydration appears to be about six times the tendency to alcoholation.

Bredig, Lapworth, Stieglitz, Acree, and others have adduced much evidence in favor of the view that it is the complex cation formed from the amide, acid, ester, etc., by the addition of the hydrogen ion which is the reactive compound. It makes no difference in the mathematical treatment of this idea or in any of the experimental work which has been

[1] THIS JOURNAL, **32**, 455.

done to test this theory, whether we assume that the ion which is added to the base be $\overset{+}{H}$, $\overset{+}{H_2OH}$, or $\overset{+}{C_2H_6OH}$. But all the work on esterification, hydrolysis, etc., has gone to show that the reaction velocities are proportional to the concentrations of hydrogen ions as determined by conductivity, etc. The same conclusion was drawn concerning alcoholysis from the data in Table II. Hence it has been assumed by those who have worked on catalysis that the ions whose concentration is measured by electrical conductivity are the agents in catalysis, and that this is true whatever the medium, otherwise such close proportionality would not hold.

If the ion, $C_6H_5CON\overset{+}{H_3}$, is to react so as to give benzoic acid and ammonia it will have to come in contact with a water molecule to do so. It is simpler to assume that the hydrated hydrogen ion simply adds to the base,

$$C_6H_5CONH_2 + \overset{+}{H_3O} = C_6H_5CO_2\overset{+}{NH_5},$$
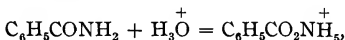
and that then this complex breaks up in course of time. It may break up into the very stable benzoic acid and ammonium ion,

$$C_6H_5CO_2\overset{+}{NH_5} = C_6H_5COOH + \overset{+}{NH_4}.$$
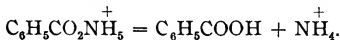
This is then the slow, monomolecular reaction. In the esterification of acids or amides the alcoholated hydrogen ion would add to the base in exactly the same way but these alcoholated complex ions would likely be even more unstable than the corresponding hydrated ions.

Mathematically, at least, it is necessary to assume the presence of at least a small number of $\overset{+}{H}$ ions. Then

$$[\overset{+}{H}] \times [H_2O] = K_{hy}[H_2O\overset{+}{H}] \text{ and } [\overset{+}{H}] \times [C_2H_6O] = K_{alc}[C_2H_6O\overset{+}{H}]$$

$$\text{and } \frac{[H_2O\overset{+}{H}]}{[C_2H_6O\overset{+}{H}]} = \frac{[H_2O] \, K_{alc.}}{[C_2H_6OK] \, _{hy}} = h \, \frac{[H_2O]}{[C_2H_6O]}.$$

This is used in the discussion below.

There may be also an equilibrium between the $\overset{+}{H}$ ions and the free base. In this case the $\overset{+}{H}$ ions would be partitioned among the three bases, water and alcohol being considered as weak bases. Lapworth[1] has discussed mathematically the question of an acid in a mixture of such weak bases.

In a mixture of alcohol and water both processes would go on side by side. According to Lapworth's ideas the hydrated hydrogen ions are inactive in esterification, etc., and only insignificant amounts of nonhydrated hydrogen ions can be present in water solutions. In this connection, at least, he seems not to consider alcoholated hydrogen ions. If we accept this, it is not easy to see why there should be such close analogy between esterification of acids in alcohol and hydrolysis of amides in water. This analogy has been assumed and emphasized by Acree and others. The present work on alcoholysis serves to bring these even closer together. Besides, we have come to regard the hydrogen ions as they exist in water solution as extremely active.

In the case of an acid, say benzoic acid, in solution in a mixture of alcohol and water, the alcoholated hydrogen ions would combine with it to form complex ions, and so too may the hydrated hydrogen ions, and in even greater numbers. The complex alcoholated ions will break up, forming the ester, but when the hydrated ones break up they can only reform the benzoic acid. In the case of an acid and its ester both in the mixture of water and alcohol, both of these processes would go on with the acid and with the ester. When the ester combined with a hydrated hydrogen ion the complex ion could break up into acid and alcohol but when it combined with an alcoholated hydrogen ion, and the complex ion is decomposed, only ester can be formed. The effect will be to establish equilibrium, as is well known. Plainly the place to study the relative numbers and reactivity of these alcoholated and hydrated hydrogen ions is with such compounds as amides with which both can react. In the case of an amide in a mixture of water and alcohol, that is,

[1] *Loc. cit.*

in the presence of hydrated and alcoholated hydrogen ions, hydrated and alcoholated complex ions will be formed and each kind will decompose according to its own rate.

We may express these ideas in the following equations, the first of which are adapted from Lapworth. In these B stands for the amide or other base.

$$(1) \qquad B + C_2H_6O\overset{+}{H} = BC_2H_6O\overset{+}{H}.$$
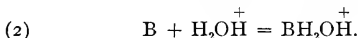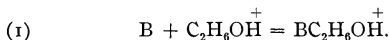
$$(2) \qquad B + H_2O\overset{+}{H} = BH_2O\overset{+}{H}.$$

Then $\quad$ (3) $\quad [B] \times [C_2H_6O\overset{+}{H}] = \frac{1}{K'} [BC_2H_6O\overset{+}{H}]$

and $\quad$ (4) $\quad [B] \times [H_2O\overset{+}{H}] = \frac{1}{K''} [BH_2O\overset{+}{H}].$

Since it is the complexes, $BC_2H_6O\overset{+}{H}$ and $BH_2O\overset{+}{H}$, which are decomposing, each at a rate peculiar to itself, if V_a be the rate of alcoholysis and V_h the rate of hydrolysis, then

$$(5) \qquad V_a = [BC_2H_6O\overset{+}{H}]K_1,$$

and $\quad$ (6) $\qquad V_h = [BH_2O\overset{+}{H}]K_2.$

Substituting from (3) and (4) we get

$$(7) \qquad V_a = [B] \times [C_2H_6O\overset{+}{H}]K'K_1$$

and $\quad$ (8) $\qquad V_h = [B] \times [H_2O\overset{+}{H}]K''K_2.$

A number of different processes may be imagined by which the same complex ions may be ultimately formed. Several of these may be in operation at the same time. Quite a number of equations and equilibria may be written expressing these. These are linked together by the relation of the K's as mentioned below. The above was selected on account of its directness and simplicity.

The above equation states that the velocity of alcoholysis equals the concentration of the base multiplied by the concentration of the alcoholated hydrogen ion, and multiplied by two constants, one of which, K', represents the tendency of

the base to combine with the alcoholated hydrogen ion, and the other, K_1, the tendency of this complex cation to decompose. A similar statement may be made concerning the hydrolysis. The $[B]$ represents, of course, not the total amount of amide put into the solution but only so much of it as is present at any given time as the free base. It is not strictly correct to suppose that the same fraction of the amide would exist as free base in different solvents with different concentrations of acid, etc.

From Lapworth's work it appears[1] that $K'' = \dfrac{K_4}{K_7 K_5}$ in which K_4 is the dissociation constant of the amidonium hydroxide, K_7 the hydration constant of the amide given by $K_7 = \dfrac{[Amide][H_2O]}{[Amide\ H_2O]}$ and K_5 the dissociation constant of water. K' is made up of a similar set of values in which alcohol replaces water.

Unfortunately most of the data needed for detailed and accurate calculations are not known. Information is needed as to the dissociation constant for alcohol, the affinity constants of the amides, both in water and in alcohol, and their tendencies to form hydrates and alcoholates, also as to the relative hydration and alcoholation of the hydrogen ions, as well as more comprehensive data as to the degree of dissociation of hydrochloric acid in mixtures of alcohol and water at various temperatures. A knowledge of the influence of viscosity, osmotic pressure, heats of dilution, etc., on reaction velocities is also required.

Acree and Nirdlinger[2] concluded that in somewhat similar concentrations, not over 4 per cent of the acetamide was present as salt in water solution. If the amount of salt formed in alcoholic solution is not greatly different, for an approximate calculation we may consider $[B]$ to have the same value in the two equations (7) and (8). From the data of Kablukoff as above discussed, it appears that at $V = 1$, hydrochloric acid in alcohol is dissociated 37 per cent, while in water, at the same volume, the dissociation is 78 per cent. Hence

[1] J. Chem. Soc., **93**, 2166.
[2] *Loc. cit.*

if we assume, as above, that all ions are alcoholated in alcohol and hydrated in water, for pure alcohol we will have for 1 N HCl $[\overset{+}{C_2H_6OH}] = 0.37$, and for pure water and 1 N HCl, $[\overset{+}{H_2OH}] = 0.78$. Green[1] has concluded that the mobility of the ions, in conductivity, varies inversely as the two-thirds power of the viscosity. Assuming, for the present, that the same relation holds as to reaction velocities, 296, the alcoholysis velocity found for benzamide, has been multiplied by $\left(\dfrac{0.00957}{0.00590}\right)^{2/3}$, 0.00957 being the viscosity of the solution in which the alcoholysis velocity was measured and 0.00590, that of the corresponding water solution in which the hydrolysis velocity was measured. This gives 408, which is assumed to be the rate at which alcoholysis would take place in a solution of the same viscosity as that in which the hydrolysis was measured. I intend measuring the effect of the viscosity of the medium on a number of these reactions, so as to have a sure basis for such calculations as this.

Then $\qquad 408 = [B] \times 0.37 \times K_1K'$
and $\qquad 234 = [B] \times 0.78 \times K_2K''$.

Taking $[B]$ as practically equal to 1 in each case, we get $K_1K' = 1103$, and $K_2K'' = 300$. These are then the velocities with which alcoholysis and hydrolysis might be supposed to take place in solutions of equal fluidity and with 100 per cent dissociation of the hydrochloric acid. They are relative, rather than absolute. Assume that the hydration tendency is h times as great as the alcoholation tendency. Then in the alcohol of Series X., in which there were 86.1 molecules of alcohol to 13.9 of water, the relative number of alcoholated and hydrated hydrogen ions would be 86.1×1 and $13.9 \times h$. Putting these in the formulae above we have

$\qquad V_a = [B] \times a \times 86.1 \times 1103$
and $\qquad V_h = [B] \times a \times 13.9h \times 300$.

Since in a given solution at a given time $[B]$, the concentration of the amide, and a, the per cent of dissociation of the

[1] J. Chem. Soc., **93**, 2049.

acid, have the same pair of values in the two equations, the relative rates of alcoholysis and hydrolysis may be obtained from these by division. But this ratio was measured and found to be 7.9 in this series, and 4.6 in Series XI. Equating these values, $7.9 = \dfrac{1103 \times 86.1 \times 1}{300 \times 13.9 \times h}$, $4.6 = \dfrac{1103 \times 75.5 \times 1}{300 \times 24.5 \times h}$. From these h comes out 2.9 for the first, and 2.5 for the second. This is intended to be simply suggestive of a line of approach.

I intend to take up this subject in a comprehensive way and by a study of these and other amides in a variety of mixtures and concentrations, I hope to accumulate data which will aid in the solution of these questions.

In returning, after ten years, to the hydrolysis of acid amides, on which I worked several years, first under President Remsen[1] and later independently,[2] I have taken up the subject with the additional light which has been thrown on the mechanism of this and other analogous reactions by the modern theories of Kastle, Euler, Bredig, Acree, Stieglitz, Goldschmidt, Lapworth and others. This has been done by arrangement with Professor Acree who was the first to study amides from the newer point of view. The alcoholysis of the amides has come up as a development of my work on hydrolysis of amides, on which I hope to report later.

Johns Hopkins University,
Baltimore, Md.,
April 7, 1909.

AN APPARATUS FOR THE EXTRACTION OF LIQUIDS WITH ETHER.

By Augustus H. Fiske.

For the purpose of extracting solutions with ether, or other low-boiling liquids, it has been customary in this laboratory, to use a simplified form of the apparatus of Van Rijn,[3] but, since the liquid to be extracted is contained in a tall, narrow

[1] This Journal, **21**, 281.
[2] *Ibid.*, **24**, 397.
[3] Ber. d. chem Ges., **28**, 2387 (1895).

vessel inside the jacket which conducts the hot vapors to the condenser, the amount which may be extracted at one time is limited by the size of the jacket to 150 or 200 cc. Having occasion to extract a liter or so of solution at a time, the following apparatus was devised, which is simpler and more efficient than any of the other extraction devices already described, so far as I can find.

The apparatus consists of a flask (A) above which is a reflux condenser (B), but between the lower end of the condenser and the flask is inserted a trap (C), from which the distillate is conducted to the flask (D) containing the solution to be extracted. The trap (C) consists of a small bulb at the mouth of the condenser tube, which catches the distillate as it runs down the walls of the tube, and draws it off without allowing it to run back into the distilling flask below. This trap is a modification of the apparatus of Boessneck,[1] which, however, requires such a large tube for the condenser that its efficiency is much impaired, and the cork over which the extracting liquid runs is a source of contamination. The last mentioned disadvantage appears as well in the apparatus of Eiloart,[2] while in the extractor of Shenstone,[3] which is less closely related to the form here described, the diameter of the condenser tube is much reduced by the gutter placed about the inner wall, and this forms a serious obstacle to the free passage of vapors from the distilling flask to the condenser. It would also appear to be a very difficult piece of apparatus to construct. In the apparatus shown, the common laboratory condenser is used, the stem of the trap being connected to the condenser by a piece of rubber connecting tubing.

The flask (D) is a common distilling flask of 500 cc. or a liter capacity, containing the solution to be extracted. The extracting solvent is led from the drain of the trap to the bottom of (D), passes up through the liquid, and then runs back through the side tube of (D) to the distilling flask (A) to be distilled again. To obviate the necessity of taking the apparatus to pieces when the liquid in (D) is to be renewed, a siphon is

[1] Chem. Ztg., **14**, 870 (1890).
[2] Chem. News, **53**, 281 (1886).
[3] J. Chem. Soc., **1883**, 125.
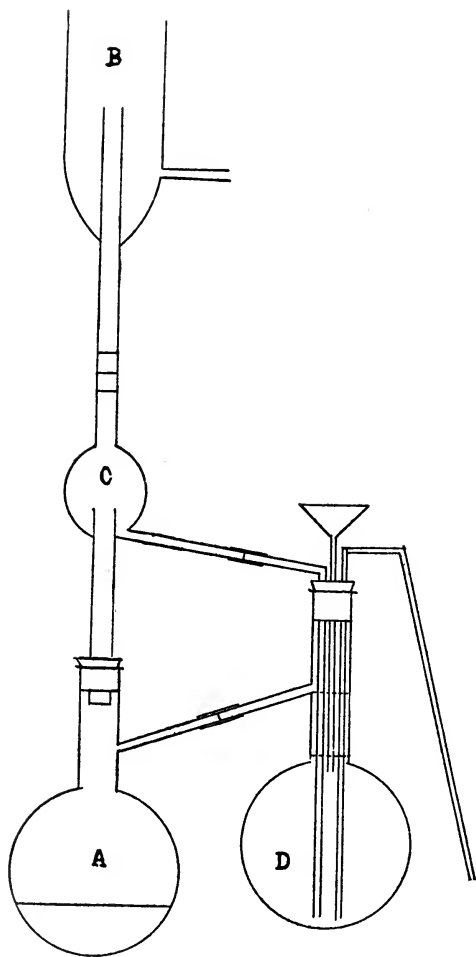
provided to draw off the spent liquid, and a funnel for re-filling. The stem of the funnel should be long enough to dip below the surface of the liquid in (D), to prevent the escape of any vapor which may find its way up the side tube from (A).

To find the relative efficiency of the apparatus, solutions of succinic acid in water were extracted with ether in it and in the Van Rijn apparatus under approximately the same conditions, and for the same length of time. After allowing the apparatus to act for $2\frac{1}{2}$ hours, in each case, the following results were obtained. The Van Rijn apparatus, holding 125 cc. of a solution containing 5.7 per cent solid succinic acid, extracted 62 per cent of the substance. The new extractor, holding 540 cc. of a solution containing 6.4 per cent solid succinic acid, extracted 67 per cent of the substance. These results were obtained under the usual conditions of work in the laboratory, and although only rough determinations, they show conclusively, that the new form of apparatus, is just as efficient, per cc. of solution extracted, as the older form, while it will extract 4 times as much solution in the same length of time. Undoubtedly the flask (D) might be increased in size to hold larger volumes of solution, without impairing the efficiency of the apparatus. There must be a limit, however, to the diameter of the flask which may be used, and still allow the extractor to work efficiently, but on reaching this limit, if still larger volumes of liquid are to be extracted, the increase in size must come in a vertical direction. The neck of the flask is a distinct advantage here, as it permits the existence of a sufficient layer of ether above the solution, without necessitating the use of a large excess which takes no active part in the work of extracting. A cylindrical vessel, therefore, should be used, which should have a neck with a side tube like a distilling flask. Neumann,[1] Eiloart,[2] Diepolder,[3] and Foerster,[4] have described cylindrical containers for the liquid to be extracted in their forms of the apparatus, but without the neck and side tube.

[1] Ber. d. chem. Ges., **18**, 3061 (1885).
[2] Chem. News, **53**, 281 (1886).
[3] Ber. d. chem. Ges., **30**, 1797 (1897).
[4] Chem. Ztg., **22**, 421 (1898).

To extract solutions of high specific gravity, the vertical difference between (C) and the level of the ether in (D) may not be enough to allow an ether column of sufficient height to force its way down the delivery tube of (C), through the heavy liquid in (D). If this is the case, the vertical distance from (A) to (C) should be increased until the column of ether in the delivery tube is sufficiently heavy to start the circulation. In the Van Rijn apparatus, it is impossible to increase the height of the ether column without reconstructing the entire apparatus. Therefore, to extract heavy solutions in this device, it is necessary to reduce the quantity of the solution, in order to get a satisfactory circulation of ether through the liquid; but in reducing the vertical height of the solution, you reduce the proportional amount of solution with which the ether comes in contact and likewise, the length of time in which the ether is in contact with the substance to be extracted. Thus the ether will have less chance to become saturated with it.

The ideal form of extractor would be one in which the length of solution through which the ether passes is sufficient to allow the ether to take up its greatest content of extractive substance, but as it takes some time for the ether to come into equilibrium with the solution, this equilibrium point is probably never approached in any extractor of this character. Therefore, it follows that the longer the ether may be in contact with the solution, the more efficient is the action of the extractor, other conditions remaining the same. As the action of the extractor depends on the relative solubility in water and ether of the substance to be extracted, then, for every individual substance, there is a different degree of saturation of the ether during the extraction, and at the same time, this equilibrium changes as the solution which is to be extracted becomes more dilute. From these considerations we can see that there can be no general rule for the height of solution to be extracted, but in order to have the extractor do its best work, we should make the solution as deep as we can, which would force the ether to come in contact with as much solution as possible, and simultaneously make it stay

in contact with the solution the greatest possible length of time. The reduction of the height of the column of solution in the Van Rijn apparatus is, therefore, very detrimental to its efficient action.

The trap (C) may also be used for the ordinary distillation of liquids, where economy of space on the laboratory desk is required. When using the trap for this purpose, a small U-shaped bend should be made in the delivery tube to form a liquid seal, thereby preventing the escape of uncondensed vapors in this direction. Various devices for distillation have been proposed by Wollney,[1] Leather,[2] Peters and Rost,[3] and Chatelan,[4] but all are more complex than the trap described above.

CAMBRIDGE, MASS.,
March 19, 1909.

RADIOACTIVITY.[5]

BY W. MARCKWALD.

I. *Electricity in Gases.*

The first suggestion of an atomic conception of electricity was furnished by Faraday's law of electrolysis, for this law found its obvious explanation in the assumption that each valence of an ion combined with the same elementary quantity of electricity. This quantity, usually denoted by ε, could be calculated and was found to be 3.2×10^{-10} electrostatic units.[6] But only with the recent discoveries as to the electric behavior of gases was a firm foundation given to this hypothesis. As is well known, gases are usually nonconductors of electricity, or at any rate it is not proved that they are ionized when unaffected by exterior influences, but they become so when acted on by light of short wave length (ultraviolet light), or when subjected to high temperature, to Röntgen rays, or to other

[1] Z. anal. Chem., **24,** 56 (1885).

[2] J. Soc. Chem. Ind., **8,** 81 (1889).

[3] Z. angew. Chem., **1896,** 485.

[4] Chem. Ztg., **25,** 612 (1901).

[5] Address delivered before the German Chemical Society, May 2, 1908, and published in Ber. d. chem. Ges., **41,** 1524. Translated by B. B. TURNER.

[6] Stoney: Belfast Meeting, Brit. Ass., **1874.** Richarz: Wied. Ann., **52,** 385 (1894).

rays which will be mentioned later. Under these circumstances the gaseous ions are driven by an electric field towards the electrodes in opposite directions with a velocity which depends chiefly on the potential difference. If this is increased, the current also increases up to a certain point, and then remains constant. The maximum current is called the "saturation current," which is a measure of the ionizing power of the rays that are acting. Theoretically, this phenomenon is explained by assuming that when the rays fall on the atoms of the gas, these give off negatively charged elementary particles, electrons, which, as well as the positively charged atoms that are left, combine with neutral molecules to form large ionic-molecular aggregates. This hypothesis explains the comparatively slow rate of diffusion of the gaseous ions,[1] as a consequence of which the ions do not move fast enough in a weak electric field to reach the electrodes before a number of them have been neutralized by oppositely charged ions. When the potential difference is high enough, however, practically all the ions reach the electrodes and the strength of the current depends solely on the source of energy which brings about the formation of new ions.

Townsend,[2] J. J. Thomson,[3] and others have measured experimentally the electric charge carried by each ion of gas, and found that the value of ε for any gas is almost identical with that for the hydrogen ion in solution, a fact whose importance for the hypothesis of electrons is obvious. However, according to Townsend's latest investigations,[4] this holds only for the negative ion, the positive ions of a gas carrying a double charge, which would imply also the splitting off of two electrons by each atom of gas.

The electric properties of gases undergo a radical change when subjected to high potential discharges at very low pressures, as in the so-called Hittorf's or Crookes's tubes. There are then expelled in straight lines from the cathode at enormous velocities corpuscles, which, before the discovery that

[1] Riecke: Ann. Phys. [4], **12**, 74 (1903).
[2] Phil. Mag. [5], **45**, 125 (1898). Phil. Trans., **193**, A, 129 (1899).
[3] Phil. Mag. [5], **46**, 528 (1898); **48**, 557 (1899); [6], **5**, 346 (1903).
[4] P. Roy. Soc., **80**, A, 207 (1908).

this was not a case of real radiation, were named cathode rays. These corpuscles are deflected both by electric and magnetic fields, and the direction in which they are deflected indicates that they carry a negative charge. From the amount of the deflection Wiechert,[1] J. J. Thomson,[2] and others were able to calculate the velocity and also the ratio ε/μ of charge to mass. The former is, on the average, about 1/10 the velocity of light, though Lenard, in his well known experiment, has been able, by passing the rays through an aluminium window, to filter out rays of greater penetrating power and having a velocity ¼ that of light. The ratio ε/μ is independent of the nature of the gas in the tube, and is likewise practically constant for rays of average velocity, amounting to about 1.8×10^7 in electromagnetic units, while the ratio ε/μ for the electrolytic hydrogen atom is approximately 10^4.

If we make the assumption, which has been established by Thomson in a way that we cannot now go into, that the charge carried by the corpuscles is equal to the atomic charge of gases under atmospheric pressure, and therefore, as we saw, equal also to the charge carried by the hydrogen ion in solution, the mass of the corpuscles is found to be about 1/1800 of that of the hydrogen atoms. Furthermore, Thomson holds that even this mass is not real, assuming rather that the corpuscles of the cathode rays, that is, the electrons, only show an apparent mass because they must possess a certain amount of inertia, in consequence of the attraction exerted by the surrounding ether. It can be calculated mathematically that the resistance to change of motion which the electron must experience as a result of this inertia will be appreciably constant as long as the velocity remains within the limits so far observed in the case of cathode rays, but that it must increase as the velocity approaches that of light, and would become infinitely great, and therefore the electron would appear to have an infinite mass, when this limit is reached. We shall find an important confirmation of this hypothesis when we come to consider the rays from radium.

[1] Abhdlg. phys.-ökon. Ges. Königsberg, **38**, 1 (1897); Wied. Ann., **69,** 739 (1899).

[2] Phil. Mag. [5], **44,** 293 (1897); **48,** 547 (1899).

If then the process of ionization is regarded as the separation of an electron from the atom, and if the electron is admitted to have an apparent mass, we are naturally led to regard the residual atom also as an aggregation of electrons. The explanation of the Zeemann effect and of the periodic system of Mendeléeff and Lothar Meyer furnished by this hypothesis can only be referred to here.

Besides the cathode rays, Goldstein discovered in the discharge through a vacuum tube another kind of radiation known as "canal rays." These travel in a direction opposite to that followed by the former rays and are oppositely deflected by magnetic and electric fields.[1] It follows that we have to do here with positively charged particles. Their velocity is only slightly less than that of the cathode rays, but their mass, as calculated from the ratio ε/μ on the hypothesis that each particle of the canal rays carries only one electric charge, is of the order of magnitude of the atoms.

A third kind of radiation outside the vacuum tube has been demonstrated by Röntgen. These rays, named after the discoverer, are produced, together with heat and light, when the cathode rays strike an obstacle. We are inclined to consider them as wavelike motions in the ether, because they are not deflected by magnetic nor by electrostatic forces.

II. *The Discovery of Uranium Rays.*

When the cathode rays strike the glass wall of a vacuum tube, a brilliant fluorescence is excited. Accordingly, shortly after the discovery of the Röntgen rays, Poincaré suggested that this fluorescence might be the source of the new rays, and that possibly all fluorescent substances emitted similar rays. This induced Becquerel[2] in the year 1898 to investigate the action of the beautifully fluorescent uranium salts, uranium potassium sulphate, for example, on the photographic plate. He found, in fact, that the salts affected the plates through light proof paper, just like the Röntgen rays. However, the same photographic effect was

[1] W. Wien: Verh. physik. Ges., **16**, 165 (1897); **17**, 10 (1898).
[2] Compt. rend., **122**, 420, 501, 559, 689, 762, 1086 (1896).

also observed when the fluorescent salts were replaced by other uranium compounds, and the effect was strongest with metallic uranium itself. As other phosphorescent substances did not affect the plates through an opaque material, Becquerel came to the conclusion that the radiation observed is characteristic of uranium and its compouuds.

The uranium rays, like the Röntgen rays, ionize gases. Being able, as we have seen, to measure quantitatively the ionizing power of such rays by means of the saturation current, as indicated by a suitable electrometer, Mme. S. Curie[1] compared the action of equal quantities of different uranium compounds distributed over equal surfaces and found it approximately proportional to the uranium content, from which she concluded that the radiation is a property of the uranium atom. This, with a certain reservation, is still held to be true at the present day.

Of the remaining elements known up to the year 1898, only one showed "radioactivity," namely, thorium, the radiating power of which was discovered almost simultaneously by C. G. Schmidt[2] and S. Curie,[3] and found to be of the same order of magnitude as that of uranium.

III. Radium and Polonium.

So much the more striking was it, therefore, that uranium minerals, as Mme. Curie found in one of her researches, showed an unexpectedly high activity. Thus pitchblende from Joachimsthal, the most important raw material in the uranium industry, though containing only about 50 per cent of uranium, surpassed this metal threefold in activity. This observation led M. and Mme. Curie to the supposition that the mineral might contain an unknown substance, with a radioactivity much greater than that of uranium. A complete analytical investigation of the pitchblende, in which each fraction separated was tested with the electrometer, confirmed this view. The bismuth which was present in the mineral to the extent of about 0.3 per cent was found

[1] Ann. chim. phys. [7], **30,** 99 (1903).

[2] Wied. Ann., **65,** 141 (1898).

[3] Compt. rend., **126,** 1101 (1898).

to be almost 100 times as active as uranium, and as ordinary bismuth is inactive, an element, unknown till then, must have been mixed with the bismuth separated from the pitchblende. The separation of this element was next undertaken, at first with very little success. The name given to it by its discoverers was polonium.[1]

In the further investigation of pitchblende, in which Bémont took part, P. and S. Curie[2] found a second very active constituent. The barium, which was precipitated in still smaller amount than the bismuth, showed about the same activity, and in this case, by means of fractional crystallization of the chloride, they succeeded in accumulating the active constituent, to which they gave the name radium, in the first fractions, and thus eventually they obtained pure radium chloride.

But before this end could be attained, many tons of the uranium ore had to be worked up. This substance is treated at the Joachimsthal mine with sulphuric acid with the addition of a little nitric acid, and the uranium salt is extracted. There remains a residue amounting to about 1/3 of the original ore, consisting chiefly of gangue, but containing also lead, copper, iron, bismuth, and other salts, among which is a very small amount of barium-radium sulphate. To separate this, the entire mass is first boiled with alkali, to decompose the sulphates. Silica and plumbic hydroxide go into solution at the same time. The residue from the treatment with alkali is extracted with hydrochloric acid to dissolve the oxides of the heavy metals and the earths. The undissolved portion is now boiled with concentrated sodium carbonate solution to convert the sulphates of barium and radium into carbonates, the liquor is carefully removed by washing, and the residue is extracted with hydrochloric acid free from sulphuric acid. The mixture of barium and radium salts is thus brought into solution and purified by the analytical methods customary in the case of barium. In this way, from a ton of Joachimsthal residues, there are obtained 3–4 kilograms of barium-radium sulphate, containing at most 0.4 gram of radium. An analytical method

[1] Compt. rend., **127**, 175 (1898).
[2] *Ibid.*, **127**, 1225 (1898).

for separating radium from barium by chemical reagents has not yet been discovered, and the preparation of pure radium salts has been achieved only by fractional crystallization of their salts. The corresponding salts of radium and barium seem to give mixed crystals in all cases, so that only by a complicated process of fractionation can the desired end be reached. According to Giesel,[1] the separation is effected most easily through the bromides.

The spark spectrum of radium has been thoroughly investigated by Demarçay,[2] Runge and Precht,[3] and others. Three very bright lines are conspicuous in the blue and violet. The flame spectrum, described by Giesel,[4] is characterized by two red bands, so that the flame of the Bunsen burner is colored intensely carmine-red by radium salts.

The atomic weight of radium has been determined by Mme. Curie[5] from the proportion of chlorine in the chloride, and in the earlier investigation, carried out with only 0.1 gram of the salt, was found, on the assumption that the formula for the chloride is $RaCl_2$, to be 225. In her later determination with 0.4 gram at her disposal, she obtained the value 226.18.

The radiating power of pure radium salts surpasses that of uranium more than a millionfold. The surprising effects which a few milligrams of these salts can produce have greatly increased popular interest in the discovery of radioactive substances. The discharge of an electroscope is effected almost instantaneously at a great distance; phosphorescent substances, as barium platinocyanide, zinc blende, diamond, willemite, and many others, are made brilliantly luminous, and the radium salts themselves phosphoresce. Many other substances, among which nitrogen and helium[6] are especially interesting, show a certain degree of phosphorescence, when subjected to the action of radium.

The photochemical effect of radium can be detected at a

[1] Wied. Ann., **69**, 91 (1899).

[2] Compt. rend., **127**, 1218 (1898); **129**, 116 (1899); **131**, 258 (1900).

[3] Ann. Phys. [4], **10**, 655 (1903); **12**, 407 (1903).

[4] Ber. d. chem. Ges., **35**, 3608 (1902).

[5] Compt. rend., **135**, 161 (1902); **145**, 422 (1907).

[6] Sir William and Lady Huggins: P. Roy. Soc., **72**, 169, 409 (1903); **76**, 488 (1905); **77**, 130 (1905). Himstedt and Meyer: Physik. Z., **6**, 688 (1905); **7**, 762 (1906).

distance of as much as 2 meters, but by long exposure much more powerful effects than that on the photographic plate are caused by these rays. Glass is colored violet or gray according to its composition. Giesel[1] has shown that the salts of the alkalies acquire the same color as Goldstein has produced in them by the action of cathode rays; common salt is colored brown, potassium chloride violet, and potassium sulphate green. Many reactions are catalytically accelerated by the radium rays, such as the formation of hydrogen chloride[2] from its elements, for instance, and the decomposition of hydrogen peroxide.[3] Air in contact with radium bromide is ozonized, a change with which is associated an interesting oxidation of the salt to hypobromite, and its conversion into carbonate under the influence of the carbon dioxide of the air.[4] From an aqueous solution of radium bromide small quantities of hydrogen and oxygen are evolved continuously, and there is always more hydrogen in the mixture than corresponds to the composition of water.[5] This fact has yet to be explained, as it has not been possible to demonstrate any accompanying oxidizing action which would account for the loss of oxygen.

The physiological action of the radium rays, which resembles very closely that of the Röntgen rays, was noticed first by Walkhoff,[6] and soon confirmed by Giesel,[7] and also by Becquerel and P. Curie.[8] If the skin is exposed for a long time to the rays, blisters and even penetrating ulcers are formed. This, and the bactericidal action discovered by Aschkinass and Caspari,[9] have led to attempts to utilize the rays therapeutically, but so far such attempts have met with doubtful success.

The energy evolved by radium was first measured calorimetrically by P. Curie and Laborde,[10] who found that 1 gram

[1] Verh. d. physik. Ges., Jan., **1900**.

[2] Jorissen and Ringer: Ber. d. chem. Ges., **38**, 899 (1905); Arch. néerland. sci. exact. nat. [2], **12**, 157 (1907).

[3] Fenton: P. Camb. Phil. Soc., **12**, 424 (1904).

[4] P. and S. Curie: Compt. rend., **129**, 823 (1899).

[5] Giesel and Bodländer: Ber. d. chem. Ges., **36**, 347 (1903). Ramsay and Soddy: P. Roy. Soc., **72**, 204 (1903). Ramsay: J. Chem. Soc., **91**, 931 (1907).

[6] Photogr. Rundschau, Oct., **1900**.

[7] Ber. d. chem. Ges., **33**, 3569.

[8] Compt. rend., **132**, 1289 (1901).

[9] Arch. physiol. Ges., **86**, 603 (1901).

[10] Compt. rend., **136**, 673 (1903).

of radium liberates in 1 hour 100 calories. According to Ångström[1] the correct value for the heat evolved is greater, namely, 117 cal., while Precht[2] obtained a still greater value, 134.4 cal. Such an evolution of heat is sufficient, as Giesel[3] has shown, to maintain the temperature in a flask containing 0.7 gram radium 5° C. above that of the surrounding medium.

In the year 1902 polonium[4] was first separated from pitchblende. Electrolytic experiments showed that the metal is far more "noble" than bismuth, so that their difference in solution tension is enough to cause the deposition of polonium on a rod of bismuth dipped in a solution of the chloride. Stronger reducing agents, such as stannous chloride, for example, precipitate it from its solution. The precipitate, which amounts to about 0.3 part per thousand of the bismuth present, consists chiefly of tellurium, from which the polonium can be separated in various ways, the most convenient being the precipitation, by excess of ammonium hydroxide, of the polonium as hydroxide from the solution of the chlorides acidified with hydrochloric acid, or the precipitation of the tellurium by hydrazine. Starting with 50 kilograms of bismuth from 15 tons of pitchblende, a nearly quantitative yield of 3 milligrams of the substance, which was certainly still impure, was obtained. These figures show that the quantity of polonium in the bismuth from pitchblende is less than that of radium in the pitchblende itself.

That these elements could be found at all is solely due to their radiating power, and the manner of their discovery reminds one strongly of the discovery of the rare alkali metals by Bunsen and Kirchoff by means of spectrum analysis. But the electrometer test for radium is a million times more sensitive than the spectroscopic test, although the spectrum of the element is very characteristic, and the radioactivity of polonium is a thousand times greater than that of radium. To give an idea of the delicacy of the electrometric method, we may

[1] Physik. Z., 6, 685 (1905).
[2] Ann. Phys. [4], 21, 595 (1906).
[3] Ber. d. chem. Ges., 36, 2370 (1903).
[4] W. Marckwald: Ber. d. chem. Ges., 35, 2285, 4239 (1902); 36, 2662 (1903) 38, 591 (1905).

imagine the above 3 milligrams of polonium electrolytically deposited on a copper band the length of the equator; then if a piece of this band 1 cm. long, that is, a 4000-millionth part were taken, its radioactivity could be detected easily with the electroscope.

A method for the separation of polonium was indicated by the periodic system, which showed a gap after tellurium in the sixth group for an element of atomic weight 210. The hypothesis that polonium belonged in this place was the means of foreseeing its chemical properties, and finding a way to separate the new element from the old.

The following figures on the separation of new elements from great dilutions are of some interest:

1 part caesium was separated from 6 million parts Dürkheim water,

1 part xenon was separated from 40 million parts air,

1 part radium was separated from 10 million parts pitchblende,

1 part polonium was separated from 5000 million parts pitchblende.

IV. Rays from Radioactive Substances.

The rays emitted by radium and polonium differ in a characteristic manner. As early as 1899 Rutherford[1] showed that the rays from uranium are complex in their character. Some of them, the α-rays, have slight penetrating power and are stopped by a sheet of aluminium 1/10 mm. thick, and since they are likewise absorbed by gases to a corresponding degree they have a strong ionizing action. The rest, the β-rays, have about 100 times as great a power of penetration, and show, in consequence, proportionally less ionizing action. Still another kind of rays, present in very much smaller proportion, the γ-rays, were demonstrated later by Villard.[2] These rays are about 100 times more penetrating still than the β-rays. Radium, uranium, and thorium emit all three kinds of rays, while polonium gives off, leaving out of account, for the present, the newly discovered δ-rays, only α-rays.

The explanation of the nature of these rays is furnished by

[1] Phil. Mag. [5], **47**, 109 (1899).
[2] Compt. rend., **130**, 1010 (1900).

their behavior in magnetic and electric fields. Giesel[1] and also St. Meyer and von Schweidler[2] were the first to show that the β-rays are deflected by a magnet in the same way as the cathode rays, and by measuring the magnetic and electrostatic deflections, Becquerel[3] showed that the β-rays from radium must be considered as cathode rays of very variable velocity. While the slower rays are about equal in velocity to those produced in a vacuum tube the fastest, and therefore most penetrating, rays have almost the velocity of light. In the case of the latter Kaufmann[4] has determined the ratio ε/μ of electric charge to mass, and found that the deduction from Thomson's electron hypothesis, that, as we saw, the apparent mass of the electrons must increase with their velocity, is confirmed by the facts.

The α-rays resemble the canal rays to the extent that their deflection by magnetic and electric fields shows them to be positively charged particles of atomic dimensions. Rutherford[5] determined their velocity and found this to be constant for each individual radioactive substance; in the case of different substances the velocity varies, as far as determined experimentally, between $1/20$ and $1/13$ of that of light. On the other hand, the ratio ε/μ is the same for all substances. It amounts to 5.07×10^3 and is therefore almost exactly half as great as in the case of the hydrogen ion. The particles must therefore be at least twice as great as the hydrogen atom, if we assume the indivisibility of the electric charge. Rutherford has put forward the hypothesis that the α-particles are helium atoms which carry two electric charges, or, otherwise expressed, have lost two electrons.

The charge of the α-rays proceeding from any source can be measured electrometrically by receiving them on a metal plate in a vacuum. As the charge of the individual α-particles is known, the number of particles emitted in unit time can be ascertained. By further determining the saturation current

[1] Wied. Ann., **69**, 831 (1899).
[2] Physik. Z., **1**, 90 (1899).
[3] Compt. rend., **130**, 206, 372, 810 (1900).
[4] Nachr. k. Ges. Wiss. Gött., **1900**, No. 2.
[5] Physik. Z., **4**, 235 (1902); Phil. Mag. [6], **12**, 348 (1906); **13**, 110 (1907).

which they produce in air, the number of pairs of ions produced by one particle can be determined.[1] This is dependent upon the velocity of the rays and, assuming that each particle carries two charges, it amounts on the average to 200,000. Quite recently Regner[2] has applied an interesting method to the problem of counting directly the particles emitted by polonium. For this purpose he made use of a phenomenon discovered by Crookes.[3] While, in general, phosphorescent substances are thrown into a state of uniform luminescence by the α-rays, as also by all similar rays, a screen of Sidot's blende, especially when examined with a lens, shows a characteristic play of sparks. Crookes explained this behavior as caused by a bombardment by the α-particles. Regner brought under the microscope a feeble polonium preparation with a screen of zinc blende in such a manner that he could count the separate flashes of light. From the saturation current produced by the same preparation he calculated the number of particles emitted, and assuming that each particle carried two charges he found in this manner numbers which agreed with sufficient accuracy.

In penetrating any medium the velocity of the α-rays is reduced without any change taking place in the proportion of charge to mass and the reduction is proportional to the square root of the thickness of the layer penetrated.[4] When the velocity has sunk to about 1/36 of the velocity of light the rays suddenly lose their power of ionizing gases, of causing phosphorescence, and of acting on the photographic plate. We have then no means whatever of ascertaining their presence; and since, moreover, the velocity of the rays emitted is, as we saw, different for different radioactive elements, it follows that the limit of their activity in air must be characteristic of each substance. For polonium, the range of activity in air under normal circumstances amounts to 3.86 cm.[5] Bragg and Kleemann[6] have shown that by means of this character-

[1] Rutherford: Phil. Mag. [6], **10**, 207 (1905).
[2] Verh. d. physik. Ges., **10**, 78 (1908).
[3] Chem. News, **87**, 241 (1903.)
[4] Rutherford: Phil. Mag. [6], **12**, 134 (1906).
[5] Levin: Physik. Z., **7**, 513 (1906).
[6] Phil. Mag. [6], **8**, 917 (1905); **10**, 318 (1906).

istic not only can the individual radioactive elements be identified in a simple manner but mixtures can also be analyzed without further trouble.

The γ-rays have been as yet comparatively little studied. They form only a small fraction of the energy emitted by radium. As they are not deflected magnetically nor electrostatically, they resemble the Röntgen rays, especially such as are produced from "hard" tubes.[1] McClelland[2] and Wiggers[3] have shown that they are not homogeneous.

That the β-rays from radium carry electric charges may be shown by a pretty experiment which was devised by Strutt.[4] A small glass tube containing radium salts is hung in an exhausted vessel and well insulated. The exterior walls of the tube are made capable of conducting by being painted with phosphoric acid, and two leaflets of aluminium are fastened to them; the negatively charged β-rays penetrate the walls of the tube, while the positively charged α-particles are kept back, whereby a positive charge is produced in the interior of the tube, and transferred by induction to the outer walls. The aluminium leaflets diverge until they touch the walls of the vacuum vessel, which are connected to the earth, when they are discharged, collapse, and the occurrence is repeated.

If polonium emitted only α-particles it would acquire *in vacuo* a negative charge, but J. J. Thomson[5] has shown that the contrary is the case. He finds the explanation in the fact that besides the α-rays there is present another kind of very slow, easily absorbed β-rays which have been called δ-rays. Their velocity is only about $1/100$ of that of light,[6] so that they can be so strongly deflected by a magnetic field that they will return in a circular path to the point from which they started. As the α-particles experience only a slight deflection it follows that in a magnetic field polonium will acquire a negative charge.

[1] Eve: Phil. Mag. [6], **8**, 610 (1904).
[2] *Ibid.* [6], **8**, 70 (1904).
[3] Z. Radioakt., **2**, 420 (1905).
[4] Phil. Mag. [6], **6**, 588 (1903),
[5] Nature, **71**, 438 (1905).
[6] Ewers: Physik. Z., **7**, 148 (1906).

V. The Hypothesis of Disintegration: Uranium and Uranium X.

Since the discovery of radioactivity, the question has been vigorously discussed as to how the new phenomena are to be brought into line with the law of conservation of energy. Numerous hypotheses were put forward to explain how radium could apparently give out its rays continuously without ever becoming exhausted and without receiving any demonstrable accession of energy from without, but none of these were satisfactory, nor did any of them further our knowledge of the nature of radioactivity. But at the end of the year 1902 Rutherford and Soddy[1] came forward with their hypothesis of the breaking down of the atoms of radioactive elements and so brought clarity into the apparently confusing abundance of contradictory observations. This hypothesis has in the meantime been so brilliantly confirmed by new experiments, of the accumulation of which it has often been the inciting cause, that its rapid success is probably unexampled in the history of science. It will therefore be well to discuss in connection with this hypothesis the development which the investigation of the radioactive phenomena has gone through in the last five years. But first let us consider the most important facts which have led to its formulation.

While the dependence of the activity of the various uranium compounds on their content of uranium made it natural to suppose that the radiation is a characteristic of the uranium atom, one observation by Crookes[2] seemed to contradict this. He was able to separate from uranium an exceedingly small quantity of a substance which acted very vigorously on the photographic plate, while the uranium that remained had lost this power. Crookes named this substance uranium X. For its separation several methods were used. If uranium nitrate containing water of crystallization is dissolved in ether an ethereal solution of the anhydrous nitrate and an aqueous layer which contains but very little dissolved salt are obtained. The whole of the uranium X is found in the aqueous solution, together with a small quantity of uranium nitrate. Another method

[1] Phil. Mag. [6], **4**, 370, 569 (1902); **5**, 576 (1903).
[2] P. Roy. Soc., **66**, 409 (1900).

for separating uranium X from uranium consists in treating the solution of uranium salt with an excess of ammonium carbonate, in which, as is well known, the precipitate first formed redissolves. The uranium X is then precipitated, together with the other impurities of the uranium, such as iron. If the original uranium salt is very pure, small quantities of impurities must be added to it to produce the precipitate.

Becquerel[1] found another way to separate uranium X from uranium, and made the more important observation that the former lost its activity in the course of a few months, while the latter regained its original activity in the same time. He could then repeat the process of separation of the active constituent as often as he pleased.

These observations were extended and corrected in an important particular by Soddy,[2] as well as by Rutherford and Grier.[3] Crookes and Becquerel had studied only the action of their preparations on the photographic plate. By means of the electroscope it was now found that the uranium, even after the separation of the uranium X, showed almost undiminished activity, and it was proved in this way that only the β- and γ-rays belonged to the uranium X, but that the uranium itself emitted the whole of the α-rays. Rutherford and Soddy[4] further studied the time-rate of the decay of the radiation emitted by uranium X, which conformed exactly to the increase of the β- and γ-radiation emitted by the uranium which remained. It decays in geometrical progression with the time, so that the original activity is reduced to one-half in about twenty-two days, to one-fourth in forty-four days, and to one-eighth in sixty-six days. The curves (Fig. I.) illustrate the law according to which the decay, or the increase, as the case may be, of the radiation, took place. If the original activity of the β-radiation of the uranium is called I_0, the activity after the time t (in seconds) I_t, then we have the equation $\dfrac{I_t}{I_0} = e^{-\lambda t}$, in which e is the base of the natural log-

[1] Compt. rend., **133**, 977 (1901).
[2] J. Chem. Soc., **81**, 860 (1902).
[3] Phil. Mag. [6], **4**, 315 (1902).
[4] *Ibid.* [6], **5**, 422 (1903).

arithms and λ a constant, the so-called "radioactive constant."
Its value amounts, in the foregoing case, to 3.6×10^{-7}, on
an average.   For the increase of the β-radiation of the uranium,
the complementary equation $\frac{I_t}{I_0} = 1 - e^{-\lambda t}$ holds.

These facts can now be simply explained if we assume that
the uranium is continuously giving up α-particles to form
atoms of uranium X, which, on their part, undergo a further
very rapid change with the loss of an electron.   What the
nature of this change may be, we can not for the present defi-
nitely say.
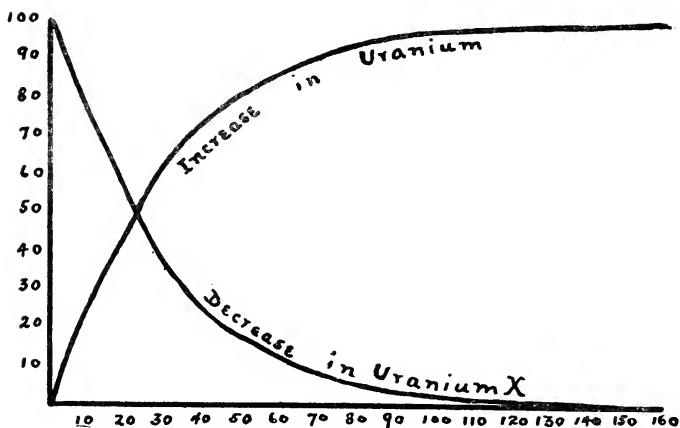
Fig. I.

If the transformation of the uranium proceeds so slowly,
in comparison with that of the uranium X, that the number
of uranium atoms present does not appreciably alter during
the period in which the atoms of uranium X, present at a
given time, are completely changed into the next stage of
their transformation, then it is evident that the uranium,
after it has been separated from the uranium X, must again

produce in this period the same number of uranium X atoms, and therefore regain its original radiating power. It is then in a state of radioactive equilibrium with its products of decomposition.

The radiating power of a radioactive element is, according to this hypothesis, proportional to the number of atoms of it which are present. If one designates the number of atoms present at the beginning by N_0, the number present after the time t by N_t, then the above equation takes the usual form for a reaction of the first order: $N_t = N_0 \times e^{-\lambda t}$.

The radioactive constant gives the fraction of the atoms which are transformed in a second and its reciprocal, $1/\lambda$, is the average lifetime of an atom of the element in question. For uranium X this has a value of 32 days. The radioactive constant is independent of the temperature within the widest limits which are accessible to observation. It is often the only safe characteristic which we have for the rapidly changing radioactive substances, the so-called metabols. But just as little as we could doubt the existence of helium when it was only known by the Frauenhofer line of the element in the sun's spectrum, just so little do we doubt the reality and individuality of a metabol which is characterized only by its activity constant.

If the radiation of a radioactive substance does not proceed simultaneously from each of its atoms, but only from those which at the moment are breaking down, then according to the theory of probability the exponential law will be true only if the number of the atoms present can be assumed as infinitely great.[1] Otherwise the intensity of the radiation from a preparation will be subject to fluctuations. E. Meyer and Regner[2] recently confirmed this consequence of the hypothesis by measuring the saturation current produced by a feeble polonium preparation, while Regner[3] obtained similar results by counting the scintillations produced by it on a zinc blende screen.

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[1] von Schweidler: Ueber Schwankungen der radioaktiven Umwandlungen, 1er Congrès Internat. Étude Radiologie et Ionization, Liège, 1905.

[2] Verh. d. physik. Ges., **10**, 1 (1908).

[3] *Loc. cit.*

VI. *The Transformation Products of Thorium.*

Even before they studied the radioactive transformation of uranium Rutherford and Soddy[1] had observed exactly similar relations for thorium, but as these relations are complicated, it seemed advisable to discuss the later investigations first. If thorium hydroxide is dissolved in an acid and reprecipitated by caustic soda it is obtained with unchanged radiating power, but if ammonium hydroxide is used, the activity of the precipitate is only 45 per cent that of the original. If the solution is evaporated and the ammonium salts driven off by ignition, an unweighable residue remains, the so-called thorium X, which possesses the remainder of the activity of the thorium. The change of radioactivity in this case occurs at first irregularly, for reasons which are now perfectly clear but the discussion of which shall be given later. The activity of the thorium diminishes on the first day and that of the thorium X increases correspondingly, but after this there occurs a regular increase of the activity of the thorium and a corresponding decrease of that of the thorium X according to an exponential law, so that after three weeks the activity of the former has regained its original value, while that of the latter has quite disappeared (Fig. II.). The life of thorium X is shorter than that of uranium X; the activity has fallen to half its value in 3.64 days.[2] This value is called its constant of half decay.

While the decomposition product of uranium X is not known, that of thorium X was discovered even before the separation of the latter from the mother element had been effected. It is the thorium emanation.[3] If air is allowed to pass over certain compounds of thorium, or through the solution of thorium salts, it carries with it a radioactive gas which is called the emanation. Its effects persist for only a very short time, the activity of the gas being reduced to one-half in 54 seconds. The gas diffuses slowly and therefore has a high density; it may

[1] J. Chem. Soc., **81**, 321, 837 (1902).

[2] von Lerch: Monats. Chem., **26**, 899 (1905).

[3] Owens: Phil. Mag. [5], **48**, 360 (1899). Rutherford: *Ibid.*, **49**, 1 (1900). Rutherford and Soddy: *Ibid.* [6], **4**, 569 (1902); **5**, 561 (1903).

be condensed at the temperature of liquid air and, like the noble gases, appears to be incapable of combination. The emanating power of thorium solutions is proportional to
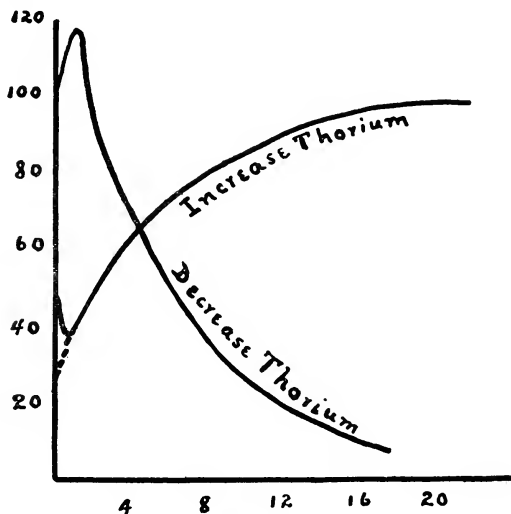
Fig. II.

their content of thorium; that of solid thorium compounds, on the other hand, varies greatly with the composition of the substances, because these occlude the emanation in varying degree. If, therefore, thorium X is separated from the solution of a thorium salt, the latter loses its power to produce emanation completely, but on the other hand the thorium X now gives off emanation very strongly. Consequently the emanation is a transformation product of thorium X.

Upon all surfaces with which the emanation comes into contact there is deposited a radioactive substance which is produced by the breaking down of the atoms of the emana-

tion. As early as 1899, P. and S. Curie[1] had observed that all objects which were placed in vessels containing radium salts became temporarily radioactive. This phenomenon they called "induced activity." Rutherford[2] noticed the occurrence of a similar phenomenon in the case of thorium and established its connection with the emanation. If the latter is allowed to pass over a negatively charged metal wire, the radioactive particles are deposited on it, while they do not collect on the wire if its charge is positive. The decomposition product of the emanation must therefore be positively charged. The particles, which are necessarily invisible and unweighable, can be rubbed off the wire mechanically, or be dissolved in mineral acids. If the acid solution is evaporated the radioactive constituent remains; the activity decays to half value with a constant of about 11 hours. In the solid thorium compound the emanation often remains occluded, as we saw above, and therefore the products of its decay must also collect in the solid. This explains why the activity of the thorium, after its separation from thorium X, at first continues to decrease, while that of the thorium X increases. The "induced activity" of the thorium remains in the thorium fraction, but decays practically completely in about one day, in which time it reaches its maximum in the thorium X, from which the emanation is being formed.

If the thorium emanation is allowed to act upon a surface only for a short time the activity given to the surface increases at first for several hours to a maximum and then begins to decrease with its normal period. Its behavior proves that the thorium activity so induced is not homogeneous, but that, on the contrary, from the first product of decay of the emanation a second is formed which is more strongly radioactive. Rutherford names these metabols thorium A and B. From the law of change of the activity of these he was able to deduce mathematically that one substance has a constant of half decay of 11 hours and the other of 45 minutes. Pe-

[1] Compt. rend., **129**, 714 (1899).
[2] *Loc. cit.* and Phil. Mag. [6], **5**, 95 (1903).

gram[1] and von Lerch[2] were able to separate partially thorium A and B because the latter is noticeably more noble than the former.

Miss Slater[3] effected a fairly complete separation by heating inside a lead case a platinum wire which had been charged with a mixture. At about 700° the thorium A began to sublime from the wire to the case; at 1000° almost pure thorium B remained on the wire, and it volatilized completely only at about 1200°. Recently Hahn[4] has shown that thorium B is not a simple substance for it gives out two kinds of α-rays. He assumes that it forms a thorium C with a very short period of decay of only a few seconds. The final product of the radioactive change of thorium is not known.

In sediments from springs in Baden-Baden, Elster and Geitel[5] found a constituent which gave off thorium emanation but did not contain a corresponding amount of thorium. The same observation has been made by Blanc[6] in the case of the sediment of other springs. Almost at the same time Hahn[7] separated from crude radium obtained from thorianite an impurity which resembled thorium completely in its chemical behavior, but was much more active than ordinary thorium. This he named radiothorium. The separation of this from thorium by chemical reagents has not yet been attained; only by producing certain precipitates in thorium solutions, for example, by precipitating iron hydroxide or barium sulphate, can a small fraction of the radiothorium be carried down.[8] Its time of half decay was found by Blanc[9] to be 737 days. Its short lifetime makes it very probable that radiothorium is an intermediate step between thorium and thorium X, and that such is the case is settled beyond doubt by the investigations of Boltwood, of Dadourian, and of McCoy

[1] Phys. Rev., **17**, 424 (1903).
[2] *Loc. cit.*
[3] Phil. Mag. [6], **9**, 628 (1905).
[4] Physik. Z., **7**, 412, 456 (1906).
[5] *Ibid.*, **6**, 67 (1905).
[6] Acc. Lincei [5], **15**, I., 328, 349 (1906).
[7] Chem. News, **92**, 251 (1905).
[8] Elster and Geitel: Physik. Z., **7**, 445 (1906). Blanc: Acc. Lincei [5], **15**, II., 90 (1906).
[9] Acc. Lincei [5], **16**, I., 291 (1907).

and Ross,[1] who found that the radioactivity of all thorium minerals is proportional to the thorium they contain.

It is altogether different, according to the same investigators, with the thorium compounds found in commerce. These all show a smaller activity than would be expected from the amount of the element present in them. The explanation of this fact, furnished by Hahn,[2] is that the thorium is not converted directly into radiothorium, but that an intermediate substance, mesothorium, which, in contradistinction to radiothorium, is removed in the separation of the thorium from the minerals, must be assumed to intervene. Mesothorium must have an appreciably longer lifetime than radiothorium because the thorium salts, after their separation from the ores, slowly lose activity, inasmuch as the radiothorium which they contain decays more rapidly than it is formed. The minimum appears to be reached in about three years and the constant of decay of mesothorium may be estimated roughly at seven years. It emits only β-rays, while the thorium which has been freed from radiothorium gives out α-rays. The following table gives the products of transformation of thorium:[3]

Name.	Time of half decay.	Kind of rays.
Thorium	$> 10^{10}$ years	α
↓		
Mesothorium	7 years (?)	β
↓		
Radiothorium	737 days	α
↓		
Thorium X	3.64 days	α
↓		
Emanation	54 seconds	α (δ)
↓		
Thorium A	10.6 seconds	β
↓		
Thorium B	55 minutes	α ⎫
↓		⎬ β,γ
Thorium C	a few seconds (?)	α ⎭

[1] Am. J. Sci. [4], **21**, 409, 427, 433 (1906).
[2] Ber. d. chem. Ges., **40**, 1462, 3304 (1907).
[3] Hahn [Physik. Z., **9**, 245 (1908)] has found recently that the β-rays of mesothorium are produced by a short-lived decomposition product, whose constant of half decay is 6.2 hours. He estimates the constant of half decay of the rayless mesothorium at 5.5 years.

VII. Transformations and Origin of Radium.

The discovery of the emanation from thorium was followed closely by that of radium emanation.[1] All solid radium compounds give out emanation only in very slight degree, but their solutions, on the other hand, emit it continuously. As this emanation has a much longer period of decay than the thorium emanation, requiring about 3.86 days to reach half value,[2] a considerable quantity of emanation thus collects in the solid substances and is suddenly set free on dissolving them, or it may also be driven out by heating the salts. On account of its comparatively long lifetime, it has been possible to study its properties thoroughly. Its velocity of diffusion has been determined many times,[3] and according to this its molecular weight would be less than 100, a value which is probably much too low; owing to the enormously great dilution at which it was determined, it is very uncertain. The gas is inert and therefore probably composed of single atoms; it may be condensed in liquid air[4] and evaporates at $-150°$. Ramsay and Collie[5] have investigated its spectrum and found certain relations to the gases of the argon group. The radium emanation emits α-rays and also δ-rays.[6]

The induced activity deposited by this emanation decays almost completely in a few hours. In dry radium salts which have been kept for a considerable time, the radium is in radioactive equilibrium with the occluded emanation and the products of its decay. If the salt is dissolved, and the solution is evaporated, the emanation is given off. The residue at first still contains these products of decay, whose radiation very rapidly dies down, and in consequence the activity of the salt at first decreases, but in a few hours reaches a minimum, at which point it is equal to only a quarter of that of the "ripened" salt, and after this increases in the course of a month

[1] Dorn: Abh. Naturf. Ges., Halle, **1900**.

[2] Sackur: Ber. d. chem. Ges., **38**, 1753 (1905).

[3] Rutherford and Brooks: Phil. Mag. [6], **4**, 1 (1902). Curie and Danne: Compt. rend., **136**, 1314 (1903). Makower: Phil. Mag. [6], **9**, 56 (1905).

[4] Rutherford and Soddy: Phil. Mag. [6], **5**, 561 (1903).

[5] Compt. rend., **138**, 1388 (1904).

[6] Slater: Phil. Mag. [6], **10**, 460 (1905).

to its original value. In the same time the emanation set free completely decomposes, although in the first hours after its separation its radiating power increases as the products of its decay increase. As the quantities of energy concerned in the case of these substances are great, Rutherford and Barnes[1] were able to follow this behavior by means of the calorimeter. As we saw before, 1 gram of radium gives out more than 100 calories in an hour, three-fourths of which large amount of energy must be ascribed to the unweighable quantities of the products of its decay existing in radioactive equilibrium with it.

Ramsay and his collaborators[2] have tried to measure the quantity of emanation produced by radium, but the values which they obtained agree so poorly among themselves and with those of other observers that these investigations are in need of confirmation. The emanation given off in 3.86 days from 1 gram of radium amounts to 1 cubic mm., according to the older experiments, and to 3.5 cubic mm., according to the later measurements. In the latter case there was observed a contraction, which is as yet unexplained, of the emanation to half its value in the course of an hour after its isolation.

The decay of radium emanation gives rise to "induced" activity, which, as in the case of thorium, consists of a series of metabols arising one from another, only in this case the series is much longer. We have said that the induced activity of radium decays very rapidly, but this is not strictly correct, as there remains at last a small residue whose activity does not noticeably decrease. This we will leave out of consideration for the present. The activity of a wire which has been exposed for several hours to the action of radium emanation decreases according to a law which may be expressed as the difference of two exponential functions, but if the action of the emanation has lasted only a few minutes the induced activity decreases at first with a constant of half

[1] Phil. Mag. [6], **7**, 202 (1904).

[2] Ramsay and Soddy: P. Roy. Soc., **73**, 346 (1904). Ramsay and Cameron: Jahrb. Radioakt., **4**, 253 (1907).

decay of 3 minutes, and after this in a very complicated manner.[1] Rutherford[2] has explained this phenomenon on the basis of the disintegration hypothesis as follows: At first there is formed from the emanation a metabol called radium A which decays with a period of 3 minutes. This emits α-rays and is changed into radium B which gives out no rays, and this in turn into radium C which gives out α-, β-, and γ-rays. The constants of half decay of radium B and radium C, for which he at first assumed incorrect values, were determined by Bronson[3] to be 26 and 19 minutes, respectively. H. W. Schmidt[4] then showed that radium B possesses a slow β-radiation, and lastly von Lerch[5] succeeded in separating electrolytically radium C from a solution of the induced activity acidified with hydrochloric acid. From this solution, free from radium C, he was able to carry down the radium B by a precipitate of barium sulphate. The rays from radium C are especially interesting because it is the only element of the radium series which produces γ-rays and it gives out its α-rays with a greater velocity than any other substance known up to this time. They can penetrate 7 cm. of air at normal pressure, while the α-rays from radium itself can traverse only half that distance.

The induced activity of radium vanishes almost entirely in the course of a day, but there remains then a very slight activity which was first observed by S. Curie.[6] Rutherford[7] has studied thoroughly this "residual activity." It shows α- and β-radiation, but neither kind of rays decreases; on the contrary, both increase and, curiously enough, according to different exponential laws, until finally they become almost constant. Rutherford explains this phenomenon by the assumption that radium C is transformed into a metabol, radium D, which gives out no rays and has a very long life-

[1] P. Curie and Danne: Compt. rend., **136**, 364 (1903); **138**, 683, 748 (1904).

[2] Trans. Roy. Soc., **204**, A, 169 (1904).

[3] Am. J. Sci. [4], **20**, 55 (1905).

[4] Physik. Z., **6**, 897 (1905).

[5] Sitzun. Wien., **115**, IIa, 197 (1906).

[6] Ann. chim. phys. [7], **30**, 289 (1903).

[7] Phil. Mag. [6], **8**, 636 (1904); **10**, 290 (1905).

time, and is transformed into radium E, which gives out β-rays. Finally, this decays, with the formation of radium F, which gives out α-rays. The time of half decay of radium D was found to be, very roughly, 40 years, that of radium E, 6 days, that of radium F, 143 days.

The lifetime of radium D could be determined only indirectly by comparison of the β-rays which are given out by the radium C and radium E from the same amount of emanation. By a similar calculation based upon the α-rays given out by radium C and radium F, St. Meyer and von Schweidler found a very different constant of half decay, 25 years.

That radium E is changed into radium F was proved by Rutherford. If the residual activity is heated to 1000° the radium F volatilizes, together with the greater part of the radium D, but radium E, which produces all the β-rays, and also the rest of the radium D remains. But radium F, which gives out α-rays, again begins to be formed and, in fact, in consequence of the short period of decay of radium E, it is formed very rapidly at first, but later on, when the radium E is largely consumed, it is formed more slowly, in proportion as the radium D already present is transformed into radium E. The radium E which remains as a residue from the heating shows a smaller constant of decay than would be given by the increase of the β-rays from the residual activity, namely, 4.5 days. This fact has been explained by St. Meyer and von Schweidler.[1] They showed that radium F is electrochemically more negative than radium E, which in turn is more negative than radium D. By electrolysis of acid solutions of the residual activity at a suitable potential difference the individual metabols can be separated from one another. In this way it is found that a precipitate giving off β-rays with a period of half decay of 4.8 days follows the radium F and is, in turn, followed by a rayless form with a period of about 6 days. As the former is formed from the latter they are named by these authors radium E_1 and radium E_2.

The most important result of Rutherford's investigations on the residual activity was the proof that radium F is iden-

[1] Lieben-Festschrift, 402 (1906).

tical with polonium. S. Curie[1] has already shown that the activity of polonium is not constant, but the decrease which she noticed was irregular, evidently because her preparation was very impure. When polonium was separated from other substances by the above-described process it was found to decay exponentially. The period of this decay has been determined many times and the most reliable observations give the constant for half decay as 139–140 days. Rutherford found, as we saw above, 143 days for radium F, St. Meyer and von Schweidler[2] 138 days, which is in satisfactory agreement with the former. The identity of the two substances is also further established by their electrochemical behavior.

Radium D is found in the lead fraction in the analytical separation of uranium ores. As it does not itself give out rays, the radioactivity of the lead obtained from the ore depends upon the transformation products of the radium D. The "radioblei" of K. A. Hofmann and Straus[3] is therefore a mixture of lead with residual activity. So far, no one has succeeded in separating radium D from lead, but Hofmann and Wölff[4] effected a certain amount of enrichment of the chloride by fractional sublimation and also still better by transforming the lead into its tetraphenyl compound.

Along with the above radioactive transformation products there is found another substance, the occurrence of which is of the greatest interest. This is helium. Rutherford considers it probable, as we saw, that the α-particles are helium atoms, and Ramsay and Soddy[5] have proved that the radium emanation, as a matter of fact, forms helium as it breaks down. This observation has been repeatedly confirmed by other observers[6] under the most various conditions of experiment. Special mention must be made of an investiga-

[1] *Loc. cit.*

[2] St. Meyer and von Schweidler: Sitzun. Wien, **114**, IIa, 389, 1195 (1905); **115**, IIa, 63 (1906). Marckwald, Greinacher, and Hermann: Jahrb. Radioakt., **2**, 136 (1905). S. Curie: Physik. Z., **7**, 146, 180 (1906).

[3] Ber. d. chem. Ges., **33**, 3570 (1900).

[4] *Ibid.*, **40**, 2425 (1907); Ann. Phys. [4], **15**, 621 (1904).

[5] P. Roy. Soc., **72**, 204 (1903).

[6] Curie and Dewar: Compt. rend., **138**, 190 (1904). Indrikson: Physik. Z., **5**, 214 (1904). Himstedt and Meyer: Ann. Phys. [4], **15**, 184 (1904). Giesel: Ber. d. chem. Ges., **38**, 2300 (1905); **39**, 2244 (1906).

tion by Himstedt and Meyer[1] which was completely free
from the objection that the helium might have been occluded
in the radium salts and have escaped with the emanation,
as the radium bromide was repeatedly distilled and the forma-
tion of helium in this salt after several weeks was then proved.
Remembering in this connection that all uranium ores con-
tain helium in large quantity, we should find in these facts
an important confirmation of Rutherford's hypothesis as to
the nature of the α-particles, were it not for the fact that re-
cent investigations throw a certain doubt upon this view.
Ramsay and Cameron[2] have caused the decomposition of
the radium emanation to take place, not, as in former ex-
periments, by itself, but in presence of water and of copper solu-
tions. There was then found no trace of helium but, instead,
neon in the former and argon in the latter case. In the cop-
per solutions there was formed at the same time lithium,
which could be recognized by its spectrum, and probably
sodium also. These most astonishing observations require,
however, further study, which has already been begun by
the authors with larger quantities of radium. The outcome
is looked forward to with the greatest expectation.

If radium decomposes regularly into α-particles and emana-
tion it must be possible to calculate its period of decay, which
is too long to be measured directly, by determining that of
one or other of its decomposition products. Now, as we have
seen, the quantitative estimation of the amount of emanation
from a given amount of radium is very uncertain. On the
other hand, the intensity of the α-radiation may be measured
with the electrometer with considerable accuracy. Assuming
that each particle carried only one charge, Rutherford[3] found
that the total number of α-particles given off by 1 gram of
pure radium, freed from its products of decay, in 1 second was
6.2×10^{10}, but on the more probable assumption that the
α-particles are helium atoms with two electric charges this
value must be halved. If we further assume that each atom,

[1] Ann. Phys. [4]. **17,** 1005 (1905).
[2] J. Chem. Soc., **91,** 1593 (1907).
[3] Phil. Mag. [6], **10,** 193 (1905).

on breaking down, gives out only one α-particle, then in 1 gram of radium 3.1×10^{10} atoms break up in unit time. Now, as is well known, the number of atoms of a substance contained in the atomic weight in grams may be taken to be 8×10^{23}. As the atomic weight of radium is 226, 1 gram of radium contains 3.6×10^{21} atoms. The fraction of these which decomposes in 1 second accordingly amounts to $3.1 \times 10^{10} \div 3.6 \times 10^{21} = 8.6 \times 10^{-12}$. This number, therefore, gives the radioactive constant of radium, from which it may be concluded that radium is half transformed in 2600 years. The accuracy of this speculation could be controlled by weighing. It is true that a radium salt, when kept in the dry state, would show only a negligible loss of weight inasmuch as the emanation formed would decompose, without escaping, into the nonvolatile metabols; on the other hand, a radium salt which was entirely unaffected by ignition—and such a substance is probably to be found in the sulphate— would lose $1/4000$ of its weight in a year.

If, then, the period of decay of radium is very small in comparison with the intervals of time with which geology is accustomed to reckon, it is still clear that this element must owe its existence in pitchblende to the much slower transformation of some other original radioactive element. The only one in question here is uranium. Consequently radium and its products of decay must be in radioactive equilibrium with this in the uranium ores. This conclusion from the disintegration hypothesis has been confirmed in the most brilliant manner by recent investigations. McCoy[1] showed that the radioactivity of all uranium ores is approximately proportional to their uranium content, but 5 to 6 times as great as the activity of the uranium that they contain. While this made it probable that the radium and uranium in these ores existed in constant proportions, this fact was established exactly by the investigations of Boltwood[2] and Strutt[3] who measured gravimetrically the amount of uranium, and de-

[1] Ber. d. chem. Ges., **37**, 2641 (1904).
[2] Phil. Mag. [6], **9**, 599 (1905).
P. Roy. Soc., **76**, 88 (1905).

termined the amount of radium by dissolving the ores, collecting the emanation, and measuring its activity with the electrometer. The proportion of uranium to radium agreed very closely in the case of most widely varying ores. Eve[1] came to the same conclusion by taking the very penetrating γ-rays of radium C as the measure of the radium contained in the uranium ores; and lastly Rutherford and Boltwood[2] determined the absolute proportion of the weight of radium to uranium in the ore in the case of a sample of pitchblende by comparing its emanating power with that of a radium solution obtained from it. They found the value 3.8×10^{-7}.

By means of this number we are now able to estimate the decay period of uranium, for if 1 gram of uranium is in equilibrium with 3.8×10^{-7} grams of radium and the constant of half decay of radium is 2600 years, then uranium must decay to half its value in $\dfrac{2600 \times 10^7}{3.8}$, that is, in 6.8×10^9 years. If this decomposition led directly to radium it ought to be easy to prove the presence of this element, for since 1 gram of uranium is in equilibrium with 3.8×10^{-7} grams of radium and the radioactive constant of radium is 8.6×10^{-12}, then 1 gram of uranium would form $8.6 \times 10^{-12} \times 3.8 \times 10^{-7}$ grams of radium in a second, that is to say, almost exactly 10^{-10} grams in a year. The amount of radium formed from 100 grams of uranium in a few weeks would be sufficient to make it possible to detect the presence of radium emanation with the electroscope. Boltwood[3] has begun experiments in this direction but has not been able to find a trace of emanation in the course of a year, although by the method he used he should have been able to detect the presence of as little as 1/1000 of the theoretical amount, and he concludes that between the short-lived uranium X, the first product of transformation of uranium, and radium, there exists at least one intermediate substance with a long lifetime.

This assumption has recently been verified in a surprising

[1] Am. J. Sci. [4], **22**, 4 (1906).
[2] *Ibid.* [4], **22**, 1 (1906).
[3] Am. J. Sci. [4], **20**, 239 (1905).

manner. No one would have supposed that in the uranium
ores which have been so zealously studied for 100 years, there
could be any other radioactive substance with appreciable
radiating power which had escaped discovery. Through a
remarkable coincidence such a substance has been discov-
ered almost simultaneously by several experimenters. The
first announcement was published by Boltwood,[1] who gave
the element the name ionium. He found it, as did also Marck-
wald and Keetman,[2] in a great number of uranium ores.
Ionium is very closely allied chemically to thorium. It gives
out α- and β-rays, the former of which are characterized by
an unusually small power of penetration, their range of ac-
tion in air being less than 3 cm. As it appears to have a
long lifetime it ought to be contained in considerable quan-
tity in pitchblende. Its proportion to radium in various
ores appears to be sensibly constant. Hahn[3] has discov-
ered ionium as an impurity in commercial preparations of
thorium. Its most interesting property, established inde-
pendently by Boltwood and Hahn, is that it produces radium
The freshly precipitated preparation, for example, gives out
no emanation, if we disregard a slight trace of thorium emana-
tion, but even after a few weeks the appearance of radium
emanation can be demonstrated.

The decay period of uranium amounts to many thousand
million years, consequently we feel hardly any greater necessity
to answer the question as to whence this element comes, than
to solve the riddle of the universe itself. We are much more
concerned with the question as to what are the final products
of the radioactive transformation process. Polonium with
its short period of decay must evidently change into a more
stable element. On the ground of hypotheses which are
very uncertain, however, Rutherford has assumed that
polonium decomposes into helium and lead. The atomic
weight of radium is 226, and as each atom of radium and
four of its products of decay, that is, polonium, the emana-

[1] Am. J. Sci. [4], **24**, 370 (1907).
[2] Ber. d. chem. Ges., **41**, 49 (1908).
[3] *Ibid.*, **40**, 4415 (1907).

tion, radium A, and radium C, give out an α-particle when they decompose, then, assuming that the α-particles are helium atoms, each product of transformation which gives out α-rays must decrease in atomic weight by that of helium, *i.e.*, by 4, and the product of decay of polonium should thus have an atomic weight of about 206 [226 — (5×4)], a value which is sufficiently close to that of lead, 206.9. The atomic weight of polonium would then be about 211, which, as we saw, would agree perfectly with its position in the periodic system, based on purely chemical grounds. These speculations found support in experiments of Boltwood's[1] on the amount of lead contained in uranium ores. He showed that not only do all uranium minerals contain lead and helium, but also that the amount of lead in such ores as, on geological grounds, must be assumed to be of the same age, is in a fixed proportion to their content of uranium, as the transformation hypothesis requires. That the same is not true of helium is no objection, since this would remain occluded to a greater or less degree according to the character of the ore.

From the decay period of uranium and the amount of lead in its ores we can, on this hypothesis, estimate the age of the ore. The primary minerals investigated by Boltwood have an age of from 400 to 2200 million years. Such minerals as gummite and uranophane, which are formed secondarily from pitchblende by external influences, can, of course, give no evidence of their age by the amount of lead they contain, but even these all contain lead. Recently, however, Marckwald and Keetman[2] have found that in 10 grams of autunite there is certainly less than 1/10 mg. of lead, if indeed it is present at all. If Rutherford's hypothesis is correct we should have to assume that the time since the deposition of the autunite in the locality in which it was found has not been long enough for the formation of noticeable quantities of lead. In other respects the activity of the autunite is

[1] Am. J. Sci. [4], **23**, 77 (1907).
[2] *Loc. cit.*

quite normal, so that uranium and radium exist in it in radio-active equilibrium.

Rutherford's hypothesis that lead is the final product of the radioactive transformation depends upon two assumptions, namely, that the α-particles consist of helium and that radium and only four of its metabols produce α-rays when they decompose. Since the latest observations of Ramsay and Cameron, this first assumption is, as we saw, no longer so certain as it previously appeared to be, when Ramsay and Soddy had proved the formation of helium from the emanation. To this we may add the fact that Greinacher and Kernbaum[1] tried in vain to establish experimentally the formation of this gas from polonium. Upon the second of Rutherford's assumptions, that only 4 metabols of radium give out α-rays, doubt has also been cast by Rutherford himself. Since the α-rays can only be demonstrated when their velocity is greater than 1/36 that of light, and since the maximum velocity of the α-particles, as in the case of radium C, is only 1/13, and their minimum velocity, as in the case of ionium, less than 1/20 of that of light, it is easy to imagine that even the so-called rayless metabols like radium D may emit slow rays. These might have half the velocity of the ionium rays without betraying their presence by causing ionization or by acting on the photographic plate. Calorimetrically, however, it ought to be possible to show their presence, if radium D were available in concentrated form. If such a slow radiation were assumed for these metabols their further transformation could be explained in the simplest way.

The question whether polonium can be transformed into lead is quite accessible to a direct experimental test. The amount of polonium obtainable from a year's output of the Joachimsthal mines should be enough for the determination of this important question. In the following table are given the transformation products of uranium with their most important characteristics:

Physik. Z., **8**, 339 (1907).

Name.	Time of half decay.	Kind of rays.
Uranium	6.8×10^9 years	α
↓		
Uranium X	22 days	β,γ
↓		
Ionium	?	α,β
↓		
Radium	2600 years	α (δ)
↓		
Emanation	3.8 days	α (δ)
↓		
Radium A	3 minutes	α
↓		
Radium B	26 minutes	β
↓		
Radium C	19 minutes	α,β,γ
↓		
Radium D	40(?) years	—
↓		
Radium E_1	6 days	—
↓		
Radium E_2	4.8 days	β
↓		
Polonium	140 days	α (δ)
↓		
Lead (?)	—	—

VIII. Actinium.

We have so far left out of account one of the radio-
active constituents of pitchblende which was discovered
by Debierne[1] shortly after the discovery of polonium and
radium.   He found it among the rare earths which are
contained in small quantities in the mineral and gave it the
name actinium.   This substance is especially characterized
by the fact that it gives out an emanation of very short life-
time.   Later Giesel[2] came across actinium in the investiga-
tion of the earths which had accumulated in the mother liquors

[1] Compt. rend., **129**, 593 (1899); **130**, 906 (1900); **131**, 333 (1900); **136**, 446, 671
(1903); **138**, 411 (1904); **139**, 538 (1904); **141**, 383 (1905).
[2] Ber. d. chem. Ges., **35**, 3608 (1902); **36**, 342 (1903); **37**, 1696, 3963 (1904); **38**,
775 (1905); **40**, 3011 (1907).

of radium bromide. Here the substance was found concentrated to a considerable extent and was named emanium, on account of its high emanating power, before its identity with actinium had been established. Giesel showed that actinium was similar to lanthanum in chemical properties but that it could be partially separated from the latter by fractional crystallization of the double nitrate with manganese. However, the separation has so far been effected only in a very imperfect manner, as in the spectrum of the product the lanthanum line alone was found. The decay period of actinium appears to be very large since it has not been possible thus far to demonstrate any decrease in its activity.

The decay period of the actinium emanation is the shortest so far observed for any radioactive substance, having a constant of half decay of 3.9 seconds, consequently the action of relatively small quantities of this emanation is exceptionally great. It can be condensed at a temperature above that of liquid air,[1] like other emanations, and emits only α-rays. It is also very striking that it is attracted by negatively charged electrodes, that is to say, it is itself charged positively like the "induced activity." This positive charge is probably likewise due to the occurrence of δ-rays. Like the radium emanation it decomposes with the formation of helium.

The induced activity of actinium decreases to half its value in about 36 minutes. Rutherford[2] and Brooks[3] showed that when the emanation acts only for a short time it forms a very feebly active deposit, whose activity rises rapidly to a maximum and then steadily falls off. The case is therefore similar to that of thorium and must be explained by assuming the formation of a rayless metabol, actinium A, from which actinium B is produced. The latter gives off α-, β-, and γ-rays. By careful study[4] of the progress of this change in activity it is found that the two metabols decay with constants of

[1] Goldstein: Verh. d. physik. Ges., **5,** 392 (1903).

[2] Trans. Roy. Soc., **204,** A, 169 (1904).

[3] Phil. Mag. [6], **8,** 373 (1904).

[4] Bronson: Am. J. Sci. [4], **19,** 185 (1905). Meyer and von Schweidler: Sitzun. Wien., **114,** IIa, 1147 (1905).

36 and 2 minutes, respectively. Actinium B is more electro-
negative than actinium A and may therefore be separated
from the latter by electrolysis of the hydrochloric acid solution
of the active precipitate. By this means it was established
that actinium B has the shorter decay period of the two.
Levin[1] separated the two metabols by taking advantage of
their difference in volatility. Actinium A volatilizes slowly
at as low a temperature as 400°, while actinium B does not
escape below 700°. Meyer and von Schweidler[2] believe that
by long action of the actinium emanation they have obtained
evidence of a further "residual activity" whose period of half
decay is 12 days, but they themselves consider the existence
of actinium C as uncertain.

The change of the actinium into emanation does not occur
directly, but there are two intermediate metabols. That
which is produced directly from the emanation was discovered
first and designated as actinium X. It is separated just like
thorium X, by precipitating the actinium from its solution
by means of ammonia. The precipitate is found to be devoid
of emanating power. The minute quantity of residue that
remains after the evaporation of the solution and after the
ammonium salts have been driven off by ignition is strongly
active and gives out emanation strongly. Its activity de-
creases with a constant of 10.2 days, while that of the ammonia
precipitate increases at the same rate.[3]

The actinium which has been freed from actinium X still
gives out α-rays, but if thiosulphate is added to this solution
there is precipitated along with the sulphur an unweighable
quantity of a substance which produces the whole of the α-
radiation, and the actinium hydroxide then precipitated from
the solution by ammonia is quite inactive. Hahn,[4] who es-
tablished this fact, named the constituent precipitated by
thiosulphate radioactinium. This substance has no power
of emanating immediately after it is precipitated, but ac-
quires the same, reaching a maximum in the course of several

[1] Physik. Z., **7**, 812 (1906).
[2] Wien. Akad. Anz., **12** (Apr. 26, 1906).
[3] Godlewski: Phil. Mag. [6], **10**, 35 (1905). Levin: *Loc. cit.*
[4] Ber. d. chem. Ges., **39**, 1605 (1906); Physik. Z., **7**, 855 (1906).

weeks, after which the activity begins to decay, decreasing to half
value in 19.5 days. The radiating power of the actinium in-
creases at the same rate. These observations prove that
the actinium itself is rayless, but decomposes into radio-
actinium, and this further forms actinium X. We obtain
in this manner the following pedigree for the decay products
of actinium:

Name.	Time of half decay.	Kind of rays.
Actinium	?	—
↓		
Radioactinium	19.5 days	α
↓		
Actinium X	10.2 days	α
↓		
Emanation	3.9 seconds	α
↓		
Actinium A	36 minutes	—
↓		
Actinium B	2.15 minutes	α, β, γ
↓		
Actinium C (?)	12 days (?)	(?)

Of the total activity of pitchblende, that of actinium and
its decay products forms only a small fraction, consequently
the question whether it occurs in all uranium ores and whether
it is present in these in a constant proportion to the uranium
they contain, is still undecided.[1] If the latter were proved
to be true it would be necessary to assume a connection be-
tween the radioactive transformation of uranium and the
formation of actinium. On the other hand, the rayless actinium
may also possess a lifetime comparable in magnitude to that
of uranium and thorium and would thus represent a third
original radioactive element.

IX. *The Radioactivity of the Atmosphere, the Earth, and Springs.*

That a charged electroscope gradually loses its charge

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[1] In a paper which has just appeared [Am. J. Sci. [4], **25**, 269 (1908)] Boltwood
makes some very interesting contributions to this question and to that of the radio-
activity of uranium ores in general, but unfortunately they appeared too late to be
considered.

in the air has long been known, but it was not until the year 1900 that Geitel[1] and Wilson[2] independently proved that this discharge must be attributed chiefly to the ions in the air. The observation that the discharging power of a closed volume of air at first increases, as must be the case, owing to the formation of induced activity, in a gas containing radium emanation, led Elster and Geitel[3] to undertake in the following year the classical experiment to determine whether the decay products of this emanation existed in the air. For this purpose they set up a wire of considerable length in the open air and charged it for many hours to a high negative potential. It was then found as a matter of fact to possess a noticeable activity which showed all the properties of induced radioactivity and especially the characteristic decay period.[4] If a wire is exposed for many days to the i.duction it is found that after the induced activity from radium has disappeared, there still remains a residue which decays with the slower period of the induced activity of thorium.[5] The amount of radioactive substances in the atmospheric air depends upon the locality and upon meteorological conditions. To account for the emanation contained in the air Elster and Geitel[6] assumed the existence of radium in the earth and confirmed this assumption, in the first place, by showing that the air in cellars, caves, and the interstices of the earth is much more strongly ionized than in the atmosphere. The carbon dioxide from springs that arise from great depths, like the helium[7] from the Tuscan fumaroles, contains considerable quantities of radium emanation.

Investigation of the earth's crust shows that as a matter of fact it possesses in all cases traces of permanent radioactivity. Clay soils,[8] as contrasted with more compact rocks, are characterized by a greater activity due to the presence of

[1] Physik. Z., **2**, 116 (1900).

[2] P. Camb. Phil. Soc., **11**, 32 (1900).

[3] Physik. Z., **2**, 590 (1901).

[4] Rutherford and Allen: Phil. Mag. [6], **24**, 704 (1902).

[5] Bumstead: Am. J. Sci. [4], **18**, 1 (1904).

[6] Physik. Z., **3**, 574 (1902); **4**, 522 (1903).

[7] Nasini, Anderlini, and Levi: Acc. Lincei [5], **14**, II., 70 (1905).

[8] Elster and Geitel: Physik. Z., **5**, 11, 321 (1904).

radium. Many volcanic rocks are much richer still in radium. Soil from near Capri showed about 1/1000 of the activity of pitchblende and the "fango" which is deposited by the hot springs of Battaglia is about equal to it in activity. From each of these Geitel[1] was able to obtain some radium mixed with barium.

The waters of springs carry off the emanation accumulated in the pores of the earth and give it up to the air according to Dalton's law.[2] Petroleum takes up the emanation in even greater quantity.[3] Many springs coming from great depths are especially rich in the radium emanation and consequently many thermal and medicinal springs have been thoroughly investigated with reference to their content of radioactive substances. The springs of Germany have been especially investigated by Himstedt, Henrich, Engler and Sieveking, H. W. Schmidt, Hinrichsen and Sahlbom; those of Austria by Mache; of England, by Allan and by Strutt; of France, by P. Curie and Laborde; of Spain, by Muñoz de Castillo; of Italy, by Nisini, Blanc and Engler; of Russia, by Sokolow; and of America, by Boltwood. Most of these springs contain only radium emanations, but some contain dissolved radium and a few thorium emanations also. For the investigation of these springs many pieces of apparatus have been described which make possible a certain and rapid determination of their activity. The most used of these is the "fontactoscope" of Engler and Sieveking.[4]

When thermal springs contain dissolved radium it is often deposited along with the slime or sinter near the point at which they rise. Like the "fango" which was mentioned above, the sediments of the springs at Nauheim, Kreuznach, and Baden-Baden are very rich in radium. These deposits sometimes contain in addition radiothorium (see above).

Although the radioactivity of many medicinal springs is

[1] Ber. d. chem. Ges., **38**, 132 (1904).

[2] Sella and Pochettino: Acc. Lincei [5], **11**, I., 527 (1902). J. J. Thomson: Phil. Mag. [6], **4**, 352 (1902). Adams: Phil. Mag. [6], **6**, 563 (1903). Himstedt: Physik. Z., **4**, 482 (1903); **5**, 210 (1904). Ann. Phys. [4], **13**, 573 (1904).

[3] Himstedt: *Loc. cit.* Burton: Physik. Z., **5**, 511 (1904).

[4] Physik. Z., **6**, 700 (1905).

certainly of no consequence with regard to their therapeutic value, it appears that in certain cases their specific principles depend upon the emanation they contain. It is known, for instance, that the hot springs of Gastein are almost free from dissolved salts, but surpass almost all known medicinal springs in the amount of emanation they contain. Now it has been shown experimentally by Loewenthal[1] that an aqueous solution of radium emanation which has no noticeable action on healthy people produces in chronically rheumatic invalids all those phenomena which are known as the "bath-reactions."

Sea water also contains radium.[2] According to Joly's[3] latest measurements the radium contained in 1 cubic meter of sea water amounts on the average to 1.7×10^{-5} mg.

X. *The Heat-budget of the Earth.*

The recognition of the wide-spread occurrence of radium in the earth makes it possible to explain a contradiction between the views of geologists and physicists in regard to the age of the crust of the earth. While geologists feel obliged to estimate the age of the earth's crust at least at 1000 million years, Lord Kelvin calculated a minimum value of 40 million years from the temperature of solidification, the geothermal gradient, and the heat capacity of the earth's surface. As we saw above, Boltwood's calculated values for the age of the uranium ores come close to the estimates of the geologists. If these are correct, there must be a continual production of heat in the earth, which has been overlooked in the calculations of the physicists. Such a source of heat is found in radium. Rutherford[4] has calculated how much radium must be contained in 1 cc. of earth to keep the temperature of the earth constant. This would require an evolution of heat amounting to 2.2×10^{-7} cal. yearly. Then, as 1 gram of radium evolves in a year more than 876,000 cal., the presence of 2.6×10^{-13} grams of radium

[1] Physik. Z., **7**, 563 (1906).

[2] Strutt: P. Roy. Soc., A, **78**, 151 (1906). Eve: Phil. Mag. [6], **13**, 248 (1907).

[3] Phil. Mag. [6], **15**, 385 (1908).

[4] Die Wissenschaft, **21**, 213 (1907).

in 1 cc. of earth would be sufficient to make up for its loss of heat by radiation. Now it has been shown by Strutt[1] in numerous investigations of the most commonly occurring rocks that the crust of the earth contains on the average about 8×10^{-12} grams radium, that is to say, about 30 times as much as the amount calculated by Rutherford to be necessary to keep the temperature of the earth constant. If we remember, moreover, that the heat evolved by uranium, thorium, ionium, and actinium has been left out of account, we see that there cannot possibly be as much radioactive substance decomposing in the interior of the earth as in the crust; otherwise the temperature of the earth would rise instead of sinking. Perhaps this contradiction may be explained by supposing that under the enormous pressure and at the high temperature of the interior of the earth the radioactive processes proceed more slowly or even in an opposite direction.[2]

XI. *The Energy Content of the Atoms.*

The radioactive decomposition of actinium emanation is 5×10^{16} times faster than that of uranium. It is therefore natural to suppose that there are radioactive substances whose lifetime surpasses that of uranium many million times. The radiation from such substances would escape detection by the electrometer. Campbell[3] and others believe that they have noticed in many metals, particularly in lead, a slight radioactivity which, it must be admitted, is barely beyond the limits of experimental error. Together with Wood,[4] he has lately announced that potassium salts show a relatively considerable β-radiation, but it is very difficult, in consequence of the widespread occurrence of radium, to prove with certainty that every trace of this and of its decay products has been excluded. Elster and Geitel[5] invariably found a slight activity in commercial lead compounds, but they were able to separate polo-

[1] P. Roy. Soc., **77**, A, 472 (1906).

[2] Lewin: Z. Elek. Chem., **27**, 390 (1907).

[3] Phil. Mag. [6], **9**, 531 (1905); **11**, 206 (1906). P. Camb. Phil. Soc., **13**, 282 (1906)

[4] P. Camb. Phil. Soc., **14**, 15, 211 (1907).

[5] Physik. Z., **7**, 841 (1906); **8**, 273, 776 (1907).

nium from them. They therefore supposed that radium D, which is closely allied to lead, is the cause of the common activity of this metal. This supposition was confirmed when they established the fact that samples of lead of great age, in which the radium D which might have been originally present would have decayed, possessed no activity.

H. Greinacher[1] has investigated the question as to whether activity may be detected in ordinary substances by means of the calorimeter. The result was negative.

It is therefore by no means proved experimentally that radioactivity is a universal property of matter, but on theoretical grounds we cannot escape the conception that no difference in principle can be assumed between the radioactive elements and other elements with regard to their energy content. One gram of radium in radioactive equilibrium with its rapidly decaying metabols evolves, as we saw, about 120 cal. an hour. If we take the average lifetime of the radium atom as 3700 years, the change of 1 gram of radium as far as radium D will set free $3700 \times 8760 \times 120$ cal. $= 389 \times 10^4$ cal., *i. e.*, as much heat as would be evolved by the combustion of 500 kilograms of coal. This amount of energy, however, is plainly only a small fraction of that which remains latent in the residual atoms.

We know of no means of accelerating the decomposition of radioactive atoms. If we had such a means we would probably be in a position to transform other elements with its help. In this way we might expect to be able to form other elementary substances of smaller atomic weights, with a simultaneous gain of enormous quantities of energy. If the change occurred suddenly it would be accompanied by the most frightful explosions, but if on the other hand we were able to regulate it at will, then we certainly could obtain from 1 kilogram of pitchblende, and perhaps even from the same weight of lead, enough energy to carry a great express steamer over the Atlantic ocean.

It was the dream of the alchemists to transform the baser into the noble metals. The radioactive substances have

[1] Ann. Phys. [4], **24**, 79 (1907).

taught us that if this process were successful there would
either be obtained thereby so much energy that in comparison
with it the value of the noble metal produced would be of
little account, or on the contrary the energy required in turn-
ing the metal into a more noble one would be so great as to
make the process perfectly valueless.

However, we do not need to wander in the realms of fancy
in order to find important and valuable questions concerning
radioactivity which remain yet to be solved. Chemical
investigation has not kept pace here with physical investiga-
tion. This can be easily understood, because chemical in-
vestigations require a greater outlay for material and are
therefore very costly. In this matter the words of Martial
will certainly prove to be true: "Sint Maecenates, non deerunt,
Flacce, Marones." (Give us a Maecenas (*i. e.*, a rich patron),
and the Virgil will not be wanting, Horace.)

REVIEWS.

THERMODYNAMICS OF TECHNICAL GAS REACTIONS. By DR. F. HABER,
Professor at the Technische Hochschule, Karlsruhe. Translated by
ARTHUR B. LAMB, PH.D. Longmans, Green, & Co. 1908. pp.
xix + 356.

The object of this book is well stated both in the preface
of the author and in that of the translator. It is a most im-
portant contribution to the general problems of thermodynam-
ics, and has special reference to the possibility of predict-
ing the course and extent of chemical reactions from a knowl-
edge of a few characteristic constants of the substances taking
part in the reaction. The work is based upon the theoretical
papers of Helmholtz and is largely the logical development
of the former's theoretical formulae. The book is divided
into seven lectures, as follows: The first lecture discusses
the latent heat of chemical reaction and its relation to reac-
tion energy. This is practically a summary of the elementary
theory of thermodynamics. The second lecture discusses
entropy and its significance in gas reactions. This chapter
contains the derivation of Helmholtz's formula and gives
several interesting illustrations and applications. In the
third lecture there is another derivation of the formula pre-
viously obtained and a discussion of its bearing on relations
between solids; in an appendix is given Nernst's addition

to the theory. The fourth lecture contains illustrations of certain reactions, such as the formation of nitric oxide, of hydrobromic acid, the water-gas reaction, etc. In the fifth lecture there are illustrations of other reactions, involving a change in the number of molecules, such as the formation of carbon dioxide, of water, of sulphuric acid, etc. The sixth lecture contains a description of the experimental methods for the determination of the specific heats of gases; and the seventh lecture discusses gaseous equilibrium and other allied subjects.

In no other text book is there such a complete treatment of the applications of thermodynamics to chemical phenomena, nor such a successful attempt to extend the theory to all classes of phenomena and to bring the data down to the most recent investigations.   J. S. AMES.

A TEXT-BOOK OF EXPERIMENTAL CHEMISTRY (with Descriptive Notes) for Students of General Inorganic Chemistry. By EDWIN LEE, Professor of Chemistry in Allegheny College. Philadelphia: P. Blakiston's Sons & Co. pp. 433. Price, $1.50.

This book is written for beginners. The author says in the preface that it "represents an effort to fuse modern views and recent advances with those older views which have stood the test, and to explain chemical phenomena in a manner which is in accord with modern chemical thought." Other recent writers have made the same effort, some with notable success.

It seems to the reviewer that Professor Lee offers too much theoretical matter and much of this too early. Two examples are offered. Chapter VII. is called "Outlines" and is intended for the teacher, not for the student; it contains a synopsis of lecture topics and *precedes* oxygen, which is the first element treated. The synopsis of formulae is as follows: "Empirical, Ex., H_2O, $C_2H_4O_2$. Rational, Ex., $HC_2H_3O_2$. Dualistic, Ex., H_2O,SO_3. Na_2O,SO_3. Na_2O, H_2O. Typical,

$$\left.\begin{array}{c}H\\Cl\end{array}\right\}, \left.\begin{array}{c}H\\H\end{array}\right\}O, \left.\begin{array}{c}H\\H\\H\end{array}\right\}N. \text{ Structural or graphic, } O\begin{array}{c}H\\\diagdown H\end{array}, N\begin{array}{c}H\\-H\\\diagdown H\end{array},$$

$$Na{-}OH, \begin{array}{c}H{-}O\\H{-}O\end{array}\diagdown S\diagup\begin{array}{c}O\\O\end{array}. \text{ Space (formulae of more than one}$$

dimension to represent the configuration of molecule.)" Dualistic and typical formulae belong to past history and are only of interest if we know *how* and *why* they were introduced. Is this a fit subject for lectures to beginners?

A chapter on solutions follows the chapters on oxygen,

hydrogen, and water. Two pages are given to surface and diffusion phenomena and to solution tension; of this a half page is filled by an abstract of a recent article by Hulett in the *Journal of the American Chemical Society*, followed by a paragraph of comment on Hulett's work quoted from Morgan. The next experiment is on osmotic pressure, with two pages of description of the work of Pfeffer and of that of Morse and Frazer on cane sugar, giving the tabulated results of the work of the latter chemists at 20° with concentrations from 0.05 to 1.00 mole per liter. Is this fit matter for a text book for beginners? Compare this with the cautious and gradual introduction of physical-chemical theory in Ostwald's "Grundlinien," in Holleman's "Inorganic Chemistry," and in Alexander Smith's "General Chemistry" and laboratory manual.

Professor Lee's book is written with an enthusiasm and love for the subject which, if helped by his own teaching, would inspire his students, but it seems to the reviewer that a thorough revision of the book is necessary to make it a success.

<div align="right">E. R.</div>

A TEXT-BOOK OF INORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Amsterdam; Emeritus Professor Ordinarius in the University of Groningen, Netherlands, and Fellow of the Royal Academy of Sciences, Amsterdam. Issued in English in coöperation with HERMAN CHARLES COOPER. Third English edition, partly rewritten. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1908. pp. 502.

The appearance of the first edition of this book was noticed in THIS JOURNAL by the present reviewer[1]. Attention was also called to the appearance of the English translation.[2] We all welcome the quick appearance of the third edition of this work in English. "The present edition represents a thorough revision of the work by both the Dutch author and the American editor. The portions on the phase rule, spectroscopy, radioactivity, iron-carbon system, and metal-ammonia compounds have been largely rewritten by the author, and the chapter on colloids, experimental determination of equivalent weights, and unity of matter, are entirely new."

The above quotation from the preface gives some idea of the nature of the revision to which the book has been subjected. The reviewer will have to differ with the translator when he says that "Notwithstanding the appearance of differential formulae in the book, it is believed that a student who is unfamiliar with the calculus should have little difficulty

[1] THIS JOURNAL, **27**, 159.
[2] *Ibid.*, **28**, 241.

in understanding the meaning and use of such formulae, provided he is willing to take the author's word for the solutions of the equations."

May the book find as large a sale as it merits.   H. C. J.

CENTENARY OF THE PUBLICATION OF AVOGADRO'S MEMOIR ON THE MOLECULAR CONSTITUTION OF GASES.

On the initiative of the Royal Academy of Sciences of Turin, a committee has been organized to provide a suitable memorial to Amedeo Avogadro to mark the 100th anniversary of the appearance of his epoch-making paper on the molecular constitution of gases, which was published in 1811. It appears to the committee that there can be no more fitting way to honor the memory of this great chemist and physicist than by the publication of a volume containing his chief works and by the erection of a monument at Turin, his birthplace and the scene of his labors.

Appeal is therefore made to all chemists and physicists in the hope that they will make it possible, by their contributions, to pay this tardy but well-merited tribute to a man as great as he was modest and to whom science owes so much. The editor of THIS JOURNAL will be pleased to receive all such contributions and forward them to the Treasurer of the Royal Academy, Via Maria Vittoria, 3, Turin.

Sen. Enrico Canizzarro is honorary president of the committee, which consists of an executive committee composed of members of the Turin Royal Academy, and a promotion committee including the presidents of the various Italian Royal Academies, Institutes, and Physical and Chemical Societies, the presidents of the London, Paris, Berlin, St. Petersburg and American Chemical Societies, the president of the Geneva Société de Physique, and a number of prominent chemists and physicists of Europe and America. The American members are named below: F. W. Clarke, W. W. Coblentz, A. Michael, A. A. Michelson, E. W. Morley, J. U. Nef, A. A. Noyes, W. H. Nichols, I. Remsen, T. W. Richards.

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